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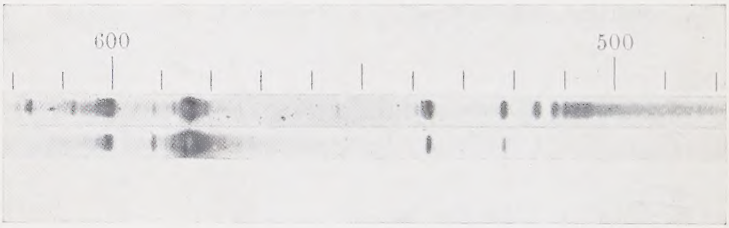

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THE SPECTROSCOPY OF THE EXTREME ULTRA-VIOLET

BY

THEODORE LYMAN, PH.D.

HOLLIS PROFESSOR OF NATURAL PHILOSOPHY, EMERITUS, IN HARVARD UNIVERSITY

WITH DIAGRAMS

SECOND EDITION

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PREFACE TO SECOND EDITION.

In the last fourteen years the extreme ultra-violet has changed from a little-known region to a well-recognized and important part of the spectrum. In this period the methods of the earlier investigators have been extended and improved and a wealth of new facts, particularly in relation to the emission spectra of the elements, have been added to our knowledge. Moreover, the region itself has been extended until at present no definite gap exists between the extreme ultra-violet and the domain of soft X-rays.

Under the circumstances it has been necessary to rewrite a considerable part of this little book in preparing a second edition.

THEODORE LYMAN.

Harvard University,
March, 1928.

PREFACE TO FIRST EDITION.

The title of this book might well have been "Spectroscopy of the Schumann Region," for it deals with that end of the ultra-violet spectrum where the absorption of air plays the determining rôle. The present title has been chosen, however, because a more extended field is necessary in order to trace the beginnings of those phenomena which become pronounced as the region beyond wave-length 2000 is explored. Thus, the absorption of the air begins to manifest itself in the ordinary ultra-violet, though it only becomes critical near

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wave-length 2000, and the absorption of many solids, usually considered transparent in the ultra-violet, begins to suffer a modification even before the region of shortest wave-lengths is reached. The book is, therefore, divided into two parts. The first and shorter portion deals with that part of the spectrum lying between wave-length 4000 and 2000; this is the region usually referred to as the ultra-violet. The second and longer portion treats of the spectrum on the more refrangible side of wave-length 2000; this is the extreme ultra-violet or Schumann region.

Some apology is due for a book whose scope is so limited. This apology must rest on the great importance which photo-electric, photo-chemical, and photo-abiotic processes have recently assumed. These effects may be observed in the ordinary portion of the spectrum, but they become much more pronounced in the Schumann region. For this reason, a knowledge of spectroscopic data, which facilitate the study of these phenomena in the extreme ultra-violet, may be considered of interest to the general scientific public.

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PART I.

INTRODUCTION.

The violet limit of the solar spectrum observed with prisms and lenses of glass appears, to the normal eye, near the Fraunhofer H lines; that is to say, in the region of wave-length 4000, if the figure is expressed in Ångström units. Early in the history of spectroscopy, however, Ritter [1] showed by experiments with silver chloride that sunlight contained chemically active rays in the region beyond the violet, and Young [2] proved that these rays were of a shorter wave-length than those commonly observed with the eye. In 1842 Becquerel [3] made a definite advance by employing a Daguerreotype plate to record the spectrum produced by a glass prism. He succeeded in obtaining pictures showing an increase in the length of the solar spectrum to the neighbourhood of a line which he called p, that is, to a wave-length of about λ 3400. At the same period, J. W. Draper [4] also photographed the solar spectrum, employing a plane grating ruled on glass, in the place of the prism. The greatest stride in the region of the ultra-violet was made by Stokes,[5] who, by using proper precautions, was able to follow the sun's spectrum to the line p with the eye, a result subsequently confirmed by Helmholtz.[6] His most striking result was due, however, to the introduction of three new methods of observation. He substituted a fluorescent screen for the Daguerreotype plate, he replaced glass lenses and prisms by a system of quartz, and he used the light from an electric spark, instead of the sun, as a source. It seems probable that he observed the strong line in the

[1] Kayser's "Handbuch," I, pp. 7 and 36.
[2] *Ibid.*, I, p. 36.
[3] *Ibid.*, I, p. 38.
[4] *Ibid.*, I, p. 39.
[5] "Collected Papers," III, p. 401.
[6] Kayser's "Handbuch," I, p. 71

aluminium spark spectrum near wave-length 1850. This limit has been surpassed only in recent years. His papers are of such importance that the reader cannot do better than to consult them in the original.[1]

The work of Miller [2] was contemporaneous with that of Stokes. He employed a photographic plate in place of the fluorescent screen, and, though his observations do not appear to extend to the farthest limit, yet his work is of interest since he noticed the transparency of water, quartz, and fluorite in the ultra-violet, and observed the transmission band of silver which has recently been so ingeniously employed by Wood.

From the year 1870 to the year 1890 there was no great advance in the knowledge of the spectrum on the more refrangible side of the limit set by Stokes, but during this period great strides were made in the spectroscopy of the ordinary ultra-violet. The subject of wave-length measurements early attracted attention. Even before the time of Fraunhofer, Young [3] made determinations of this character; but it was not until nearly fifty years later that Esselbach [4] measured the wave-length of some of the Fraunhofer lines by means of Talbot's bands. The first systematic work in this field was done by Mascart [5] in 1863, while the beginning of the classic research of Ångström [6] dates from about a year later. The invention by Rowland [7] of the concave grating, in 1882, enabled him to construct a map of the solar spectrum which surpassed in accuracy anything that had been previously produced and which yielded important standards of wave-length.

The attention which the ultra-violet received was largely due to the fact that the terrestrial sources of light, such as the arc and spark discharge, are particularly rich in radiations of a quality more refrangible than those which affect the human eye. It has resulted from the activity in this field that the spectra of the elements between wave-lengths 4000 and 2000 have been very carefully studied and the position of their lines has been accurately determined.

[1] "Collected Papers," III, p. 267, and IV, p. 203.
[2] Kayser's "Handbuch," I, p. 103. [3] *Ibid.*, I, p. 7. [4] *Ibid.*, I, p. 71.
[5] *Ibid.*, I, p. 109. [6] *Ibid.*, I, p. 110. [7] *Ibid.*, I, p. 121.

The limited character of the solar spectrum as compared with the spectra obtained from various terrestrial sources early attracted attention. The cause of the phenomenon was studied by Crookes,[1] by Piazzi Smyth,[2] and finally by Cornu.[3] They attributed the limit of the solar spectrum to the absorption of the earth's atmosphere. This result was not only important in itself, but it was also the indirect means of setting on foot work in the extreme ultra-violet. For Schumann,[4] having substituted fluorite for quartz, and having perfected a special kind of photographic plate, was stimulated by the researches of Cornu to construct his vacuum spectroscope. It was with this instrument that he discovered the region which bears his name.

The substitution of a concave diffraction grating for prisms and lenses of fluorite enabled the author to push the limit of the spectrum considerably beyond the point reached by Schumann. More recently Millikan, by the use of a special type of source, has extended the domain of the extreme ultra-violet to the verge of the region of soft X-rays.

In looking back over the foregoing paragraphs, it is at once obvious that the factors which have controlled our knowledge of the ultra-violet end of the spectrum are, first, the absorption of solids; second, the means by which the refracted light was detected; third, the character of the source; and fourth, the absorption of the constituents of the air. By way of introduction to the Schumann region, therefore, it will be well to pay special attention to the behaviour of these agents in the ultra-violet.

The classic works on spectroscopy require at the outset a detailed account of apparatus, but in the limited scope of the present volume it will be necessary to confine ourselves to those instruments which are not described elsewhere. Thus, as prism and grating spectroscopes are fully treated in many places as far as the ordinary ultra-violet is concerned, notably in Kayser's "Handbuch" and Baly's "Spectroscopy," it will not be necessary to mention them until the Schumann region

[1] Kayser's "Handbuch," I, p. 45.
[2] *Ibid.*, I, p. 50.
[3] *Ibid.*, I, p. 117.
[4] *Ibid.*, I, p. 126.

is reached. On the other hand, since instruments for the comparison of the energy given by two sources of light in the ultra-violet are not quite so familiar to the scientific reader, and since the principles involved in them often permit their use in the extreme ultra-violet, we shall begin by some description of them.

CHAPTER I.

PHOTOMETERS.

The Photographic Plate.

The function of all spectro-photometers may be divided into two distinct parts: the first consists in analysing the light from the sources into juxta-posed spectra, the second is concerned with the comparison of the relative intensity of the spectra so formed.[1] Spectro-photometers which are to be used in the ultra-violet must be provided with a dispersive system especially adapted to the region, and with a mechanism for comparing intensities of the required sensibility.

The comparison of intensity may be carried out by one of three methods. First, by the use of a photographic plate; second, by the photo-electric cell; and third, by measuring the heat energy with a bolometer, a radiometer, or a thermo-junction.

When the dry plate is employed, the relation which connects the density of image with the intensity of the light and the time of exposure, is obviously of great importance. If i_1 is the intensity of the light which falls on the negative and i_2 the intensity of the light which leaves it, the opacity is defined as $\frac{i_1}{i_2}$ and the density or blackening is the logarithm of this quantity. So that if S is the density, $S = \log \frac{i_1}{i_2}$. The connexion between the intensity of the light and the time of exposure has been written by Schwarzschild, $I t^p = \text{constant}$, where p is a constant, or very nearly a constant for normal illumination. Stark[2] has proposed the form $S = \log (k I^m t^p)$.

[1] Kayser's "Handbuch," III, p. 45.

[2] L. Geiger, "Ann. d. Phy.," 37, p. 68, 1912.

An excellent example of the simplest manner in which photographic plates may be employed in photometric measurements is afforded by the recent work of Fabry and Buisson [1] on the absorption of ozone. What follows is quoted almost word for word from the original article.

The only correct method of using photography is to attempt to produce two images of equal density on the same plate and with the same time of exposure. One of these images is produced by the light which has traversed the absorbing body under examination, the other is produced by light which has not suffered absorption but has been decreased in intensity in a known ratio. This ratio measures the amount of light transmitted by the body under examination.

In a particular case, which will serve as an illustration, the slit of the spectroscope was 1 mm. long and 0·5 mm. wide; thus the image of each ray in the spectrum of the mercury lamp, which served as a source, was represented by a small rectangle on the photographic plate. A single exposure with the absorbing medium in the light path was made on the same plate with numerous others, without absorption but with successive decreasements of intensity, the time of exposure being the same in all cases. The weakening of the light was brought about by suitable rectangular diaphragms applied to the exit surface of the last prism of the spectroscope.

After the plate was developed, the opacity of each of the images for a given ray in the spectrum was measured by a microphotometer. This instrument was especially designed to examine small areas on a photographic plate.[2] The measurement was made by comparing the opacity of the image under examination with that of a calibrated wedge of glass. As one cannot hope that the image obtained through the absorbing medium will be found identical with one of the images obtained when the light has suffered a known weakening, it is necessary to seek by interpolation for the size which the diaphragm should have had in order to realize this equality. It is found that, if the logarithm of the intensity of the light which acts

[1] "Journal d. Phy.," 3, p. 196, 1913.

[2] Fabry and Buisson, "Comptes Rendus," 156, p. 389, 1913.

on the plate is plotted as abscissa (or the logarithm of the breadth of the diaphragm, which comes to the same thing) and the corresponding densities as ordinates, a straight line will result. By means of this straight line the necessary interpolation may be accurately carried out. Thus, it is possible to calculate what diaphragm should have been employed in order to secure an exact identity of photographic action. The net result of the process is to give the ratio of the intensities of the light after the beam has passed through the absorbing medium, to the intensity before it suffered absorption. The only assumption involved is that, if the time of exposure is kept constant, equal intensities produce equal effects.

Simon [1] has invented a spectro-photometer based on the same principles. In this instrument, the intensity of the light which has not suffered absorption is decreased in a continuous manner, while at the same time the photographic plate is moved in such a way as to receive an impression of correspondingly decreasing intensity. Recently the apparatus has been improved by Defregger.[2]

An example of a method of this general character as applied to the ultra-violet is furnished by the work of Harrison.[3]

Henri and Wurmser [4] have carried on spectro-photometric measurements by a method of equal densities. Here the time of exposure is varied until the density of the image produced by the direct beam is equal to that resulting from the light which has suffered absorption. The procedure involves a definite form of Schwarzschild's rule, namely, that $S = \log kI^n t^n$, which, for the case of equal densities, yields $\frac{I_1 t_1^n}{I_2 t_2^n} = 1$, a relation which, though not rigorously exact, is probably sufficiently accurate. In this method, as in the previous one, all the observations are recorded on the same plate.

If the intensities to be compared are recorded at different epochs on separate plates, no matter what care is taken to

[1] Kayser's "Handbuch," III, p. 45.
[2] "Ann. d. Phy.," 41, p. 1012, 1913. [3] "Phy. Rev.," 24, p. 466, 1924.
[4] "Journal d. Phy.," 3, p. 305, 1913.

secure uniformity of development, some error may affect the result. Moreover, if the intensity of one beam of light is cut down by a revolving sector, the irregular illumination which results may cause an error in Schwarzschild's rule which is difficult to correct.

A short account of the factors which control the density of the image on a photographic plate may be found in Chapter XI of Nutting's "Applied Optics." It is important to remember that the "chromatic sensibility of all ordinary plates is sensibly uniform throughout the ultra-violet and down through the violet and blue of the visible spectrum to about wave-length 5000." On the ultra-violet side we shall see that the sensibility rapidly falls off as the Schumann region is entered.

Before leaving the subject of photographic spectro-photometry mention must be made of an ingenious instrument described by Nutting,[1] in which the light from each of the two sources under examination is made to produce a system of interference bands. The arrangement is such that the bright bands of one system fall upon the dark bands of the other. When the intensities of the two sources are equal, the bands disappear. The method is not applicable in the extreme ultra-violet because of the absorption of the polarizing apparatus employed.

In the spectro-photometer employed by Krüss [2] a fluorescent screen replaced the photographic plate. The instrument does not seem to have been extensively employed. It is doubtful if the fluorescent ocular possesses any advantages over other forms of detectors in the ultra-violet. Diffuse light is troublesome, and the fluorescence of the lenses and prisms forms an added difficulty.[3]

Photo-electric Cell.

The discovery by Hertz in 1887 that, if a spark gap was illuminated by ultra-violet light, the passage of the spark was

[1] "Phy. Rev.," 16, p. 129, 1903; also Königsberger, "Zeitsch. fur Instrumentenkunde," 21, pp. 59, 129, 1901.

[2] *Ibid.*, 23, pp. 197, 229, 1903.

[3] Hagen and Rubens, "Ann. d. Phy.," 8, p. 2, 1902.

facilitated, led to the investigation of the phenomenon by Hallwachs.[1] He showed that, if a cleaned surface of zinc is charged negatively, the charge is quickly lost when the surface is illuminated by ultra-violet light. This so-called photo-electric effect has been the subject of many researches. The magnitude of the phenomenon has been found to depend primarily upon the nature of the surface which is illuminated and upon the intensity and wave-length of the exciting light. It appears that many metals are particularly sensitive to the more refrangible end of the spectrum, and that the electric current which may be obtained from a particular metal is proportional to the intensity of the light which falls upon it. These facts have led to the use of photo-electric cells in photometry, and particularly in the ultra-violet region.

The exactitude of the proportionality between the current and the light intensity is obviously fundamental. It has been studied by several observers and has been confirmed for the alkaline metals by Elster and Geitel [2] for a considerable range of intensities. They employed a variety of sources, including a mercury lamp, but they did not analyse the light into its component colours. The spectral range was limited by the transparency of the "uviol" glass of which their cell was made. The accuracy of their results has been questioned; but more recent investigations show that if proper precautions are taken the photo-electric cell may be used with confidence, at least in the visible.[3]

Though the relation has not been tested for monochromatic light in the ultra-violet, it seems reasonable to believe that it holds, at least approximately, in the most refrangible part of the spectrum. However, before the matter can be considered settled, some experiments with monochromatic light of various wave-lengths beyond λ 3000 should be tried.

Kreusler [4] was among the first to employ the photo-electric

[1] "Wied. Ann.," 33, p. 301, 1888.

[2] "Phy. Zeitsch.," 14, p. 741, 1913; 15, p. 1, 1914.

[3] "Astrophysical J.," 43, p. 9, 1916; also "Bulletin Nat. Research Council Wash.," 2, p. 83, 1921.

[4] "Ann. d. Phy.," 6, p. 412, 1901.

effect in ultra-violet photometric measurement. He used a spectro-photometer in which the light, after analysis by a prism system, fell upon a platinum button contained in a vessel filled with hydrogen at a pressure of 200 mm. This button was charged to a high negative potential, the current which flowed from it to a neighbouring anode was taken as a measure of the intensity of the light which fell on the platinum. Kreusler checked the current-intensity relation for various parts of the spectral field in which he worked. He states that, if care was taken not to charge the cathode too near the sparking potential, the relation held. He determined the absorption coefficient for a number of substances between λ 3000 and λ 1850.

Meyer,[1] in 1903, employed the apparatus of Kreusler to determine the absorption of ozone, a subject which will be considered in its place. Krüger and Moeller,[2] in 1912, replaced the platinum button by a form of photo-electric cell which had been perfected by Elster and Geitel. In this arrangement a surface which receives the illumination is of potassium; it is enclosed in a vessel containing hydrogen or helium at a low pressure. Hughes [3] has described a sodium cell which is particularly well adapted to ultra-violet photometric work.

It appears that the photo-electric cell, because of its sensitivity, offers some important advantages over the ordinary photographic plate,[4] if proper precautions are taken, for work in the ultra-violet.[5] The selenium [6] cell, which has been used with advantage in photometric work in the visible, is probably too insensitive in the ultra-violet to be of much value.

Measurement of Heat.

The four instruments most commonly employed to measure the heat energy in the spectrum are, the bolometer of Langley, the radiomicrometer of Boys, the improved radiometer of

[1] Meyer, "Ann. d. Phy.," 12, p. 849, 1903.
[2] "Phy. Zeisch.," 13, p. 729, 1912. [3] "Phil. Mag.," 25, p. 679, 1913.
[4] Meyer and Rosenberg, "S.A. Vierteljahrsch. Astron. Gesell.," 48, p. 210, 1913.
[5] "Phy. Zeitsch.," 15, p. 1, 1914.
[6] "Proc. Roy. Soc.," A. V., 89, p. 75, 1913.

Nichols, and the linear thermopile of Rubens.[1] These instruments have been largely employed in the less refrangible part of the visible and in the infra red, because the maximum of heat energy for many sources lies in these regions. It was observed by Pflüger, however, that the spark and arc spectra of most metals possess sufficient energy in the ultra-violet to make their use possible.[2] If, therefore, the source is properly selected, some form of radiometer may be employed in photometric measurements even in the more refrangible region. The thermo-element of Rubens appears to be the smallest, simplest, and easiest to operate of all the radiometers, though even in its improved form it does not possess the sensibility of the bolometer or of the instrument perfected by Nichols.

A considerable number of investigators have used the thermopile in the ultra-violet. Hagen and Rubens [3] employed it in their work on the reflecting power of metals; their measurements extended to wave-length 2500. Pflüger,[4] by its use, studied the energy distribution in the spectra of various sources. He found the maximum of energy in the aluminium spark spectrum at λ 1860, and even obtained an indication of the energy of the aluminium spark in the Schumann region itself. He also [5] employed the same instrument in a straight photometric investigation in which he determined the absorbing power of a number of substances.

Pfund [6] has used the thermopile to study the reflecting power of a number of substances in the region of the very shortest wave-lengths. The thermopile has also been employed to measure the energy in photo-chemical and photo-electric researches in the ultra-violet. The work of Richardson [7] affords a good example of such an investigation.

[1] Nutting, "Outlines of Optics," chap. ix.; Coblentz, "Bull. Bureau of Standards Wash.," 9, No. 1, p. 7.

[2] "Ann. d. Phy.," 13, p. 890, 1904.

[3] *Ibid.*, 8, p. 1, 1902.

[4] *Ibid.*, 13, p. 890, 1904.

[5] "Phy. Zeitsch.," 5, p. 215, 1904.

[6] "Journal Optical Soc. Am.," 12, p. 467, 1926

[7] "Phil. Mag.," 26, p. 549, 1913.

As an instrument for photometric measurement in the ultra-violet, the thermopile does not possess the simplicity of the photographic plate or the sensitivity of the photo-electric cell. But, as its indications depend upon the energy which falls upon it without respect to wave-length, the results obtained with it are easy of interpretation.

CHAPTER II.

ABSORPTION OF SOLIDS.

Since transparency is a fundamental requisite of substances which are to be used for lenses and prisms in the ultra-violet, it is necessary to consider the absorption of the various materials available for such optical work. The ordinary kinds of glass, which serve so well in the visible, are not at all suited for the more refrangible part of the spectrum. In general, heavy flint glass is less transparent than light flint, and this, in turn, is less transparent than crown.[1] A thickness of 1 cm. of even the best of this last-named material absorbs very strongly indeed, in the region of λ 3100. Pflüger [2] has made accurate measurements with his thermo-junction photometer for a number of glasses down to wave-length 3570, and Krüss [3] has carried the measurement farther with a spectrophotometer fitted with a fluorescent screen; the most transparent material which he investigated was a borosilicate crown, 1 cm. of this permitted only 8 per cent of the light to pass at wave-length 3090. The firm of Schott, at Jena, have turned their attention to the making of glass particularly transparent to the ultra-violet. Zschimmer has published some of the results attained in a series of papers. In one of these,[4] the properties of three kinds of "uviol" glass are described and their behaviour relative to other forms of glass is illustrated by three spectrograms. It appears that a specimen of this new glass 1 cm. thick will transmit 50 per cent of the light at λ 3050, and if the thickness is reduced to 1 mm.,

[1] Kayser's "Handbuch," III, p. 377.
[2] "Phy. Zeitsch.," 4, p. 429, 1903.
[3] "Zeitsch. f. Instrumentenkunde," 23, pp. 197 and 229, 1903.
[4] *Ibid.*, 23, p. 360, 1903.

50 per cent is transmitted at λ 2800. For a thickness of 2 mm., the limit of the spectrum appears at λ 2850 for " uviol " flint, and at λ 2800 for " uviol " crown, whereas for English borosilicate crown, the limit is at λ 2970. To illustrate the transparency of the new glass for extremely thin layers, a spectrum taken through a common microscope cover glass is compared with one taken through a " uviol " cover glass. In the first case the spectrum stops at λ 2850, in the second at 2480. It is interesting to note that Zschimmer has succeeded in making a glass which is quite transparent at λ 2800, but which absorbs in the visible blue.

In later papers Zschimmer discusses the relation between the physical properties of glass and its chemical constitution [1] and the relation between its transparency in the ultra-violet and its chemical constitution.[2] In this later paper, the author points out that boric oxide (B_2O_3) and silica oxide (SiO_3) in their pure state are very transparent even beyond λ 2000, that the addition of metallic oxides lessens the transparency, that sodium oxide (Na_2O) acts more strongly in this respect than potassium oxide (K_2O), and lead oxide very strongly indeed. It has since [3] been shown that B_2O_3 is less transparent than quartz of equal thickness in the ultra-violet. Fritsch [4] has described a glass composed of six parts of commercial calcium fluorite ($CaFl_2$) and fourteen parts of B_2O_3 which he tested and found transparent to wave-length 1850. No practical use seems to have been made of this substance, perhaps because it cannot be obtained in pieces of sufficient size and homogeneity.

Recently the increasing interest in the therapeutic value of ultra-violet radiations has stimulated manufacturers both in the United States and abroad to produce glasses transparent to light of short wave-length. An idea of the success attained may be gathered from the results of tests made by the Bureau of Standards at Washington on some specimens

[1] " Zeitsch. f. Electro. Chem.," 11, p. 629, 1905.
[2] " Phy. Zeitsch.," 8, p. 611, 1907.
[3] Lyman, " Astrophysical J.," 28, p. 52, 1908.
[4] " Phy. Zeitsch.," 8, p. 518, 1907.

produced by the Corning Glass Company of Corning, New York.[1] One sample of colourless glass (G. 980 A.) 2 mm. thick transmitted 15 per cent at wave-length 2100 and 90 per cent at wave-length 3100. Another sample (G. 986 A.) is nearly opaque in the visible yet quite transparent in the ultra-violet.

On the other hand, the transparency of some of these glasses for ultra-violet light decreases considerably after they have been exposed to the sun's rays or to the radiations from a mercury lamp.[2]

It appears from what has just been said that, though these glasses offer a notable improvement over older forms, yet even they are not suitable if work is to be carried on in the extreme ultra-violet.

Among the substances which occur in nature in sufficiently large homogeneous masses to be of optical value, and which seem to promise the necessary transparency, are Iceland spar, quartz, rock salt, and fluorite.[3]

The measurements of Pflüger[4] yield perhaps the most satisfactory data on these substances. Iceland spar is easily ruled out of court. In a thickness of 1 cm. for wave-length 2800, it absorbs 15 per cent; at wave-length 2140, 97 per cent. Quartz is a far more satisfactory substance. Pflüger found considerable differences to exist between various specimens. In general, more light was absorbed when the path was parallel to the axis than when it was perpendicular. For a piece 1 cm. thick he gives the following values :—

	λ 2220	2140	2030	1860
per cent absorbed	5·8	8	16·4	32·8

He found fused quartz far less satisfactory; a plate 2·8 mm. thick permitted nothing below λ 2000 to pass. It seems probable that the effect was due to the presence of some impurity, for it will appear later that, though fused quartz is less

[1] H. P. Hood, "Science," 64, p. 281, 1926.

[2] "Technical News Bull. Bureau of Standards Wash.", No. 126, p. 4, Oct., 1927.

[3] Kayser's "Handbuch," III, p. 380.

[4] "Phy. Zeitsch.," 5, p. 215.

transparent than the crystalline variety, yet it is possible to find specimens which are quite transparent to light of much shorter wave-length than λ 1850. Both Pflüger's measurements and some qualitative observations made by Schumann [1] tend to ascribe to crystalline quartz rather less transparency than it really possesses in the region below λ 1850.

Tsukamoto [2] has recently investigated the transparency of quartz by a photographic method; for a crystalline specimen 1 cm. thick he gives the following results :—

	λ 2192	2150	2026	1860
per cent absorbed	1·1	3·6	13·7	24·4

The transparency of this particular specimen is therefore greater than that given by Pflüger. It is to be noted, however, that even for crystalline quartz the transparency varies considerably from specimen to specimen.

For a certain piece of fused quartz 1 cm. thick Tsukamoto gives the absorption at λ 2182 as 33 per cent, and at λ 1860, 83·6 per cent. On the other hand, Joos [3] claims that a piece of fused quartz 6 mm. thick showed as good transparency as a piece of crystalline quartz of like thickness, down to wave-length 1980.

The considerable differences in absorbing power observed with various specimens of fused quartz may account for the variation in efficiency which different investigators have obtained with the mercury arc in quartz when light of the very shortest wave-length was in question.

There also may be a loss of transparency when the material is exposed to ultra-violet light for long periods of time.

For rock salt, Pflüger gives 4·5 per cent absorption at λ 2800 and 30 per cent at λ 1860. Because of its high dispersion he recommends the use of rock-salt prisms protected from the action of the air by thin quartz plates cemented with glycerine. Such an arrangement is useful only on the less refrangible side of λ 2300, where the absorption of the cement

[1] "Wien. Ber.," 102, IIa, p. 415, 1893.
[2] "Rev. D'Optique," 7, p. 89, 1928.
[3] "Phy. Zeitsch.," 25, p. 376, 1924.

does not enter. He gives the following values of the angle of refraction :—

λ	Fluorite.	Quartz.	Salt.
1850–2310	3° 5′	5° 40′	27° 10′
2310–3400	2° 20′	4° 20′	10° 10′

Pflüger's values for the absorption of rock salt have led to the assumption that it is more transparent in the Schumann region than crystalline quartz. This is not the case ; absorption very rapidly sets in on the more refrangible side of λ 1800.

Of all substances fluorite is the most transparent in the extreme ultra-violet ; it is the only substance of which prisms and lenses can be constructed for work in the Schumann region. Pflüger states that at thickness of 1 cm. it absorbs 20 per cent at λ 1860. It appears that this estimate is rather too high. The greatest differences in transparency occur even among specimens of clear colourless fluorite. The whole subject will be treated in a later chapter.

Short tables giving the index of refraction for a variety of substances may be found in Baly's "Spectroscopy," 3rd Edition, Vol. I., pages 80 *et seq.*

Absorption of Gases.

In the ordinary part of the spectrum, the absorption of the air has little influence on terrestrial spectroscopic investigations ; but when the Schumann region is reached, it plays the determining rôle. The first measurements of the air's opacity, however, were not made in the extreme ultra-violet and were not concerned with a terrestrial source. Ever since quartz apparatus and the photographic plate have been used in the study of the sun's light, it has been observed that its spectrum became suddenly weakened near λ 3000, and that all trace of it was lost at a point not much farther toward the violet.

Cornu [1] suspected that the extent of the spectrum depended on the absorption of the layer of air through which the rays passed, and that the limit receded toward the red as the thickness of the layer increased. To test his hypothesis, he

[1] "Comptes Rendus," 88, pp. 1101 and 1285, 1879 ; 89, p. 808, 1879 ; 90, p. 940, 1880 ; 111, p. 941, 1890.

made observations at Courtenet (alt. 170 m.), in which he took a succession of photographs of the solar spectrum with the sun at various altitudes above the horizon. His results may be illustrated by the following values :—

Time. hr. min.	Limiting Wave-length. λ	Time. hr. min.	Limiting Wave-length. λ
10 30	2955	3 9	2990
0 2	2950	3 40	3045
1 18	2955	4 17	3045
1 50	2970	4 38	3070

He found that, if the limiting wave-length and the logarithm of the sin of the sun's altitude were taken as co-ordinates, these numbers yielded a straight line. The results were expressed by the empirical formula, $\sin h = \cdot 49 \times e^{-0\cdot 08330(\lambda - 300)}$ where h was the sun's angular distance above the horizon and where the wave-length was expressed in $\mu\mu$ (1 $\mu\mu$ = 10 Ångströms). This relation clearly suggested the absorption of the atmosphere as the factor which limits the solar spectrum.

Cornu used these results in connexion with the theory in order to establish a general relation between the thickness of the absorbing layer and the last visible wave-length.[1] Starting with the relation $P = J_\lambda F(\lambda, t)$, where P is the intensity of photographic action, J_λ, the intensity of the light of wave-length λ, and $F(\lambda, t)$ is an unknown function of the wave-length and the time of exposure, he made use of the fact that, if light of intensity J_λ traverses a plane layer of thickness D and transparency A_λ, the resulting intensity J'_λ may be expressed $J'_\lambda = J_\lambda A_\lambda^{\,D}$, where D can be written $\frac{\sin h}{l}$. These two relations led to the expression $\frac{\sin h}{l} = \psi\,(w, T, \lambda,)$, where l is the thickness of the absorbing layer at the place of observation, w the photographic activity at the limit of the spectrum, and T the constant value of t used throughout the experiments. He then compared this theoretical equation with the empirical expression derived from experiments with the sun at various heights above the horizon. He was thus enabled to write equation (1) of the form $\frac{\sin h}{l} = \frac{M e^{-m(\lambda - \lambda_0)}}{l_1}$, where λ and λ_0 are

[1] Kayser's "Handbuch," III, p. 337.

the wave-lengths corresponding to thicknesses of the absorbing layers of air l and l_1; M and m have the values derived from experiment, namely, 0·49 and 0·08330. To put this relation in a practical form, it is necessary to note that l is proportional to the atmospheric pressure p where p varies with the height above sea-level according to the equation $p = p_0 e^{-\frac{z}{z_0}}$. The equation then takes the form

$$(2)\quad \sin h = \mathrm{M} e^{-m(\lambda - \lambda_0) - \frac{z - z_1}{z_0}}.$$

To learn the effect on the limit of the spectrum of increase in altitude of the observer, the exponent of e may be set equal to a constant, remembering that z_0 denotes the height of the atmosphere at sea-level, z_1 the height of the place of observation, and λ_0 the limit of the spectrum at sea-level, the relation $dz = -mz_0 d\lambda$ results, which becomes $dz = -\cdot 0833x$ (7963 $d\lambda$) or $dz = -663{\cdot}3\ d\lambda$. The meaning of the equation being that, to increase the length of the spectrum by 1 $\mu\mu$ or 10 Ångström units, the observer must ascend 663·3 metres. Cornu [1] tested this relation by making observations at 660 metres and at 2570 metres. The results were not in exact accord with the formula, for he found an increase of 1 $\mu\mu$ for every 868 metres in elevation. However, when he redetermined the value of the constant m at the altitude of 2570 metres from observations of the sun at various times of day, the empirical relation became $dz = 896{\cdot}3\ d\lambda$, an expression which seemed in good agreement with facts.

Equation 1 has also been employed by Cornu [2] to determine the limit of the spectrum which would be set by the absorption of a terrestrial air column of constant density. In this case, sin h may be considered as unity and the formula becomes

$$\frac{l}{l_1}\mathrm{M} = e^{m(\lambda - \lambda_0)}.$$

His calculations indicate that it would require 10 metres of air to cut off the spectrum at λ 2118, 1 metre at λ 1842, and 10 cm. at λ 1566. As a matter of fact, these results

[1] Loc. cit. [2] "Comptes Rendus," 89, p. 808, 1879; 111, p. 941, 1890.

are not in agreement with experiment. As will be shown presently, the absorbing action of the air cannot be represented at all in the region between λ 2200 and 1800 by Cornu's formula.

For some time the investigations which have just been described were interpreted to mean that the limit of the solar spectrum could be entirely explained by the absorption of an homogeneous atmosphere whose density was distributed according to the barometric law. In recent years this point of view has been considerably modified.

Miethe [1] and Lehmann determined the limit of the solar spectrum at various altitudes from near sea-level to 4560 metres, with an instrument in which the photographic plate was most carefully protected from the action of stray light. They arrived at the startling result that the position in the spectrum of the last trace of light action was independent of altitude. The following numbers exhibit their data :—

Place.	Altitude. Metres.	Limit. λ
Assuan	116	2915·5
Berlin	50	2912·6
Zermatt	1620	2913·6
Gornergrat	3136	2911·0
Monte Rosa	4560	2912·1

They observed that, although the position of the last light action does not change with the altitude, the distribution of intensity near the end of the spectrum suffers some modification. Thus, by an increase of 900 metres above the altitude obtained by all previous observers, they succeeded in photographing two lines, λ 2919·8 and λ 2916·7, which, though they lay in the region within the extreme limit, had never been seen before. This change of intensity in the region near the end of the spectrum was perhaps the phenomenon studied by Cornu and to which his equations may still apply.

Their conclusion that the last trace of light action is independent of altitude has been confirmed by Wigand.[2] He employed the same spectroscope as Miethe and Lehmann, and, by means of a balloon, he reached a height of 9000 metres

[1] "Ber. Berlin Akad.," 8, p. 268, 1909.
[2] "Phy. Zeitsch.," 14, p. 1144, 1913.

and maintained his position for two hours. At this extraordinary altitude the last trace of the sun's spectrum occupied the same position on the photographic plate as it did on the earth's surface at Halle. At 9000 metres the observer has about $\frac{2}{3}$ of the mass of the air under him. As we shall see presently, there is good evidence that the absorbing gas resides in the very uppermost layers of the earth's atmosphere. It is likely then that the agent which limits the spectrum is different from that which produces the fluctuations of intensity observed by Cornu.

The limit found by Wigand for the last trace of light was λ 2897; the fact that this limit was somewhat below that observed by Miethe and Lehmann is due to a colour screen which lessened fog and so permitted more exact measurement.

In the summer of 1912, Dember [1] made observations with a quartz spectro-photometer, fitted with a photo-electric cell, at an altitude of 4560 metres. He states that the last action of the sun's rays was at λ 2800. He attributes the gain of nearly 100 units over the limit obtained by other observers to the superior sensitiveness of the photo-electric cell over the photographic plates. Owing to the unfavourable weather conditions, his observations were all made in a day and a half, and it is not perfectly certain that scattered light was completely eliminated. The results appear to need confirmation.

In considering the relative importance of the various constituents of the atmosphere as judged by their absorbing power in the ultra-violet, carbon-dioxide and nitrogen may be discarded at once, for they appear to be practically transparent in the ultra-violet.[2] Water vapour cannot be dismissed quite so easily, though its small absorption in the ultra-violet renders it improbable that it is an important factor in determining the limit of the solar spectrum.

The activity of oxygen as an absorbing agent is very great in the region under consideration. Liveing and Dewar [3] as long ago as 1888 made experiments with a tube 18 metres

[1] "Abhand. Nat. Wiss. Gesell.," "Isis," Dresden, 2, p. 1, 1912.
[2] Kayser's "Handbuch," III, p. 353.
[3] "Phil. Mag.," 26, p. 286, 1888.

long filled with " ordinary oxygen." They raised the pressure of the gas to 90 atmospheres in some of their experiments and observed that, under these circumstances, all light of wave-lengths shorter than λ 3360 was cut off. A tube of oxygen of 18 metres with the pressure of 90 atmospheres gives about the same mass of the gas as is contained in the atmosphere, but they noted that the intensity of the absorption bands in the visible produced by the compressed gas was far greater than that of the corresponding bands in the solar spectrum with a low sun ; the limit of the spectrum is also considerably higher than that obtained by Cornu in the afternoon, i.e. λ 3070. One might conclude from this, either that part of the absorption which they observed was due to some impurity in their gas, or that the oxygen in the air is not uniformly distributed. The latter supposition is equivalent to saying that their experimental tube contained more oxygen than exists between an observer at sea-level and the sun. It is quite probable that oxygen at this point in the spectrum does not obey Beer's Law, that is to say, the absorption is not a simple function of the product of the pressure and the gas path.

In connexion with what is to be presently considered, it is interesting to note that Liveing and Dewar tried oxygen in a tube 165 cm. long at pressures of 85 and 140 atmospheres, and attempted to find the extreme ultra-violet limit of the absorption band ; but though they searched the spectrum to the region of λ 2320, they could find no sign of a transmission of light. The limit of the spectrum with 85 atmospheres pressure was λ 2664 ; with 140 atmospheres, λ 2704.

From this work of Liveing and Dewar it seems likely that oxygen may play some part in the absorption of the ultra-violet end of the solar spectrum. However it is not the most important factor, in all probability.

It has long been known that ozone [1] possesses a strong absorption band in the very region under examination.[2] Quantitative measurements of this band have been made

[1] Kayser's " Handbuch," III, p. 361. Hartley, " Nature," 39, p. 474, 1889.
[2] Ladenburg and Lehmann, " Ber. Deutsch. Phy. Gesell.," 4, p. 125, 1906.

by Meyer [1] with the photo-electric arrangement of Kreusler already referred to, by Krüger [2] and Moeller with a photo-electric cell, and by Fabry [3] and Buisson by the photographic method already described. The results of Krüger and Moeller do not agree at all well with the other observers, but the values for the coefficient of absorption a defined by the relation $J = J_0 10^{-ah}$, obtained by Meyer, are in fair agreement with those of Fabry and Buisson, at least in the region

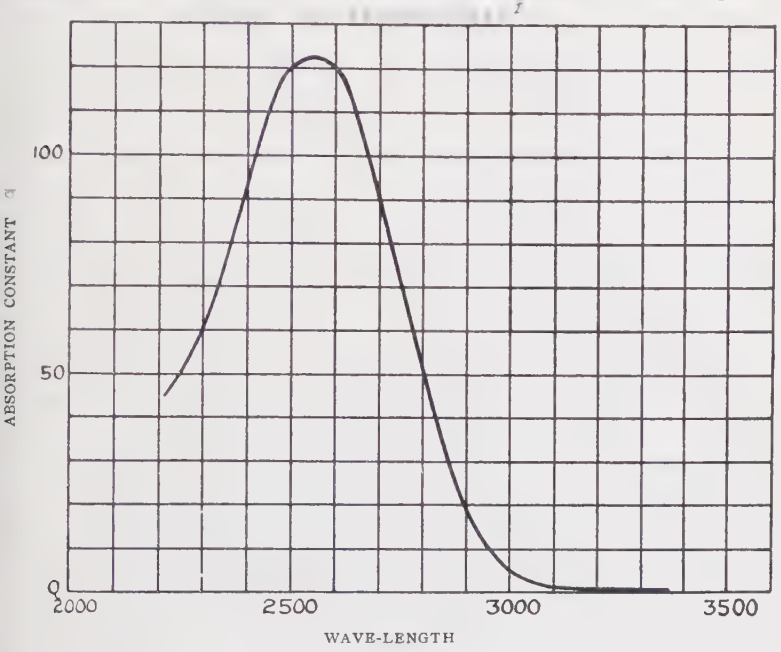

FIG. 1.

between λ 2300 and λ 2700. The values are shown plotted in Fig. 1. It appears that at λ 2600 the ratio of the values of Meyer to those of Fabry is as 126 to 120, at λ 2700 as 116 to 91 ; at longer wave-lengths the ratio is greater: at λ 2900, as 38·6 is to 16, and at λ 3000, as 30 is to 4·6. The fact that Meyer's photo-electric arrangement was comparatively insensitive in the region of longer wave-lengths while the

[1] "Ann. d. Phy.," 12, p. 849, 1903.
[2] "Phy. Zeitsch.," 13, p. 729, 1912.
[3] "Journal d. Phy.," 3, p. 196, 1913.

photographic plate is particularly efficient in this region, makes it probable that the values of Fabry and Buisson are the better of the two for the less refrangible part of the curve.

Both the observers have applied their data to the problem of the atmospheric absorption. Fabry and Buisson have shown that their relation between the absorption coefficient and the wave-length in the region between λ 2900 and λ 3300 may be transformed into a relation connecting the last visible wave-length and the absorbing thickness, identical in form with that deduced by Cornu from his best experiments on the sun at various hours of the day, and that, not only is the form of the equation the same, but the coefficients which determine the change of the spectral limit with change in altitude of the sun are of the same order of magnitude in both cases, the values being 177 and 200. They infer from this agreement that the absorption phenomena observed by Cornu are due to the presence of ozone somewhere in the earth's atmosphere.

In a continuation of their research, Fabry and Buisson [1] have measured the intensity of the solar spectrum at a number of points near the limit for various altitudes of the sun. They assume that the observed absorption may be ascribed to three causes : first, to the action of some gas whose nature it is their object to determine ; second, to molecular scattering ; and third, to the effect of fog. Of these agents the first two are evidently functions of the wave-length ; they assume that the third is not. They calculate the absorption coefficient due to scattering in a manner which is indicated presently, and they eliminate the third factor by algebraic process depending on the assumption just mentioned. As a result they are able to compute from their experimental data the absorption coefficients of the unknown gas for the various wave-lengths in question.

They state their conclusions in nearly the following words : These computed values are to be compared with the coefficients of absorption of ozone, the substance which is suspected as the

[1] " Journal d. Phy.," 2, p. 197, 1921.

cause of this absorption. If they follow, as functions of the wave-length, the same law as the coefficients of ozone, one can affirm that it is indeed this gas which is present in the atmosphere and which would cause the absorption under investigation.

As a result of this line of reasoning and experiment, Fabry and Buisson feel certain that it is to ozone that the limit of the solar spectrum is due.

Their method, moreover, permits these investigators to calculate the equivalent thickness of the ozone at atmospheric pressure which would produce the required absorption; they arrive at a value of 3 mm.

Dobson and Harrison,[1] by a modification of the method just described, have measured the amount of ozone in the earth's atmosphere, and have studied its fluctuations. Their value for the equivalent thickness of ozone is in good agreement with the figure just quoted.

The question next arises as to the distribution of the absorbing gas. Fabry and Buisson conclude from their observations that it cannot be located in the solar atmosphere. The ozone may then be either uniformly distributed in the earth's atmosphere, or it may form a layer at a relatively high altitude. There are three sets of observations which render uniform distribution extremely unlikely. In the first place we have seen that there is very little change in the extent of the solar spectrum with change in altitude up to 9000 metres; in the second, the results of de Thierry [2] based on chemical analysis of the atmosphere near the earth's surface and at 3050 metres, and those of Lespieau [2] made at different altitudes up to that of Mont Blanc, seem to indicate that the ozone content is at best only about $\frac{1}{10}$ of that required to give the observed absorption. To be sure some experiments of Pring [3] would lead to the conclusion that there is ample ozone at fairly low levels to produce the desired effect, but it seems probable that these observations are not free from error.

[1] "Proc. Roy. Soc. Lond.," 110, p. 660, 1926.
[2] "Journal d. Phy.," 8, p. 126, 1927.
[3] "Proc. Roy. Soc. Lond.," 90, p. 204, 1914.

Lastly, there are two papers which bear on the subject. In the first, Strutt [1] reports that he has been able to observe the mercury line at λ 2536 transmitted with appreciable intensity through a column of air 6·45 kilometres in length; in the second, Schaeffer [2] records a similar observation. It is not difficult to prove that these results demand a transparency far greater than would be possible were the computed mass of ozone uniformly distributed throughout the atmosphere.

Recently Cabannes and Dufay [3] have made experiments to determine the position of the layers of absorbing gas responsible for the limit of the spectrum; their results point to an altitude of from 45 to 50 kilometres.

So much, then, for the limit of the solar spectrum; its position is to be ascribed to ozone situated at a great height above the earth. Cornu's observations on the fluctuations of the limit with change in the sun's altitude may be reconciled with this view, but his conclusions on the effect of change of altitude of the observer cannot be so reconciled. These latter observations must either be considered erroneous, or the phenomena in question must be due to some cause other than a layer of ozone of limited distribution.

It remains to inquire what factors determine the transparency of the earth's atmosphere in the ultra-violet for light from a terrestrial source. If, for the present, the discussion be limited to the region between wave-lengths 4000 and 2000, it is safe to say that molecular scattering will play an important part, and that the absorption of oxygen may be a factor. In this connexion the paper of Schaeffer just mentioned is of interest. In this research the relative absorption of different parts of the Cadmium spectrum between wave-lengths 3600 and 2500 was studied when the observer was separated from the source by distances as great as 8 kilometres. A quartz spectrograph with an objective prism was employed; the densities of the various images on the photographic plate being compared photometrically. As a result it appears that

[1] "Proc. Roy. Soc. Lond.," 94, p. 260, 1918.
[2] "Proc. Am. Acad.," 57, p. 365, 1922.
[3] "Journal d. Phy.," 8, p. 125, 1927.

molecular scattering will not account for the attenuation of the shorter wave-lengths from distant terrestrial sources; some other agency is also at work, but its exact nature is at present unknown.

The air in such thicknesses as are usually present in apparatus in the laboratory exerts no appreciable absorption in the ultra-violet.

When the region on the more refrangible side of λ 2000 is entered, however, this statement no longer holds true. Schumann [1] showed that a very strong absorption sets in near λ 1850. Up to this point the transparency is greater than that predicted by Cornu, but beyond that wave-length it is far less. The whole matter will be considered in detail in a later chapter; for the present, it will suffice to state that oxygen has been shown to be the active agent involved, the result being due to an unsymmetrical band extending from the region at λ 1900 to the neighbourhood of λ 1300. So steep is the rise of this absorption that, while the line λ 1940 may be photographed through 14 metres of air, the region beyond λ 1750 is entirely absorbed by an air column 1 cm. long. The change of the absorption coefficient with wave-length has not been determined for this interesting oxygen band. The only numerical data are those of Kreusler,[2] who found that a column of air 20 cm. long absorbed 8·8 per cent at λ 1860, while at λ 1930 no absorption could be detected.

The relation of the absorption of oxygen in the neighbourhood of λ 3300, observed by Liveing and Dewar with a long column at a very high pressure, to the strong absorption of the gas in the Schumann region in short columns at atmospheric pressure, is an interesting question.

The scattering effect of the molecules of the air has already been mentioned. The percentage of light transmitted through a gas layer of thickness H containing N molecules per cu. cm. is given by the expression e^{-KH} where K is given by Rayleigh's formula,

$$K = \frac{32\pi^3}{3} \frac{(\mu - 1)^2}{N\lambda^4}.$$

[1] Kayser's "Handbuch," III, p. 338. [2] "Ann. d. Phy.," 6, p. 412, 1901.

Schuster [1] used these relations to compute the percentage of light transmitted for various wave-lengths, and arrived at a set of values for the visible spectrum in good agreement with the numbers for the transmission of the air obtained by Abbot on Mount Wilson on a clear day. He concluded that for the visible spectrum, with the exception of a slight indication of selective action in the red and yellow, atmospheric absorption is practically accounted for by the scattering of the molecules of the air.

The treatment has been considerably extended by other observers. King [2] has improved the formula for molecular scattering and has applied it to the experimental data, with an excellent agreement between theory and observation. Fowle,[3] having introduced a correction for the action of water vapour, has applied King's formula to the most recent data for the transmission of the atmosphere, and has also obtained excellent agreement to λ 3700. The experimental figures for these comparisons are obtained at such stations as Mount Wilson and Mount Whitney, which, on account of elevation above sea-level, are free from the complicating action of dust.

Reflecting Power of Metals.

The use of mirrors and reflecting gratings in the ultra-violet makes measurements of the reflecting power of metals in the more refrangible part of the spectrum of great importance.

Hagen and Rubens [4] employed a direct photometric method, in which the beam, after reflection from the surface under examination, was compared with the beam which had not undergone reflection. As has been already mentioned, they used a thermopile as the detecting instrument. The angle of incidence was about one degree; an arc served as source; the ultra-violet limit was at wave-length λ 2500. These results may be summarized as follows :—

[1] "Theory of Optics," 3rd ed., p. 320.
[2] "Trans. Roy. Soc. Lond.," A, 212, p. 375, 1913.
[3] "Astrophysical J.," 38, p. 392, 1913.
[4] "Ann. d. Phy.," 8, p. 1, 1902.

A fresh silver mirror reflects excellently in the visible, falls to a sharp minimum of about 4 per cent at λ 3160, and then rises to 34·1 per cent at λ 2510; the trend of the curve is upward at this point.

The reflecting power of platinum is steadily downward throughout the whole spectrum; it reaches 33·8 per cent at λ 2510. If the curve held its direction, about 28 per cent reflection might be expected at λ 2000. Gold sinks to a broad minimum between λ 3500 and λ 4000; it reflects 38·8 per cent at λ 2510. The curve appears to be rising at this point.

The curve for copper is roughly similar to that of gold. The minimum of reflection is thrust toward the violet, but 25·9 per cent of light is reflected at the more refrangible limit, and the upward slope of the curve in the extreme region is small.

Nickel and iron resemble platinum; they both decrease steadily in reflecting power from the limit of the visible; they reflect 37·8 per cent and 32·9 per cent respectively at wave-length 2510.

Among alloys, Mach's Magnalium (69 Al + 31 Mg) shows a constant and high reflecting power of about 83 per cent out to the limit of the visible. From there, it falls to 67 per cent at the experimental limit and the tendency of the curve is downward. It possesses a much higher reflecting power than any other known substance in the neighbourhood of wave-length 2500; it is also distinguished by the permanence of its surface.

Schröder Alloy No. 1 (66 Cu + 22 Sn + 12 Zn) and Schröder's Alloy No. 6 (60 Cu + 30 Sn + 10 Ag) closely resemble each other: they both reflect about 60 per cent at the limit of the visible and then fall off steadily to about 40 per cent. The curves tend rather sharply downward.

Brandes-Schünemann's Alloy (41 Cu + 26 Ni + 24 Sn + 8 Fe + 1 Sb) reflects but 50 per cent at the limit of the visible and 35·8 per cent in the extreme violet. Finally, Ross's Alloy (68·2 Cu + 31·8 Sn) reflects 56·4 per cent at wave-length 4000, and 29·9 per cent at wave-length 2500. So steep is the slope that a reflecting power of less than 18 per

cent might be looked for at wave-length 2000 if the curve maintained its downward course. It is extremely important to note, however, that the Brashear Alloy used for the diffracting grating with which the spectrum has been pushed to the extreme limit of the Schumann region, resembles that of Ross. It seems likely, therefore, that the reflection curve for Ross Alloy suffers a minimum and then rises again in the region of extremely short wave-lengths. At all events, it is evident that it is not safe to predict the behaviour of metals in the Schumann region from data obtained on the less refrangible side of wave-length 2500.

The condition of the polarization of the light reflected from metallic surfaces may be determined by the measurement of two quantities, the relative phase retardation and the ratio of the amplitudes of the two components vibrating at right angles to each other. A knowledge of these quantities permits the index of refraction and the coefficient of absorption to be calculated, and these, in turn, may be so combined as to yield the percentage of light reflected at normal incidence.

The method devised by Voigt rests on procedure of this kind.[1] It was used first by Minor [2] and more recently by Meier.[3] The former carried the work as far into the ultraviolet as λ 2265. He studied steel, cobalt, copper, and silver. The data for steel show a fair agreement with the numbers of Hagen and Rubens. For silver, the agreement is all that could be expected when the differences introduced by the condition of the surface are borne in mind. It is interesting to note that Minor finds a decreasing reflecting power for silver beyond the region of λ 2500; thus, at this wave-length 25 per cent is reflected, at wave-length 2265 only 18 per cent is reflected.

Meier determined the optical constants of gold, nickel, iron, platinum, bismuth, zinc, selenium, mercury, iodine, a silver copper alloy, and "Wood's fusible bismuth alloy." He followed the spectrum to wave-length 2573. The differences between his values and those of Hagen and Rubens are quite

[1] "Phy. Zeitsch.," 2, p. 303, 1901. [2] "Ann. d. Phy.," 10, p. 581, 1903.
[3] *Ibid.*, 31, p. 1017, 1910.

considerable in the ultra-violet, a fact which perhaps may be attributed to differences in surface conditions. For example, with gold he finds 27·6 per cent at the spectral limit as against 38·8 per cent obtained by the direct method; for platinum, 37·1 per cent as against 33·8 per cent; for nickel, 30·7 per cent as against 37·8 per cent. Meier followed the reflective power of mercury only to wave-length 3255. At this point he obtained 65·7 per cent. It is interesting to note that for "Wood's alloy" (exact composition not given) he obtained a higher reflecting power in the extreme ultra-violet than from any other metal which he studied, namely, 56·6 per cent at wave-length 2749 and 52·7 per cent at 2573. As the alloy appears to be easily prepared, these figures may be of practical importance.

Pfestorf [1] has recently measured the reflecting power of copper, silver, zinc, manganese, silicon, nickel and steel, from λ 6000 to λ 2500. He finds 64 per cent of the light reflected at λ 2500 by silicon.

Hulburt,[2] using a concave grating to analyse the light, a photoelectric cell to measure the intensity, and an angle of incidence of 18°, has examined the reflecting power of twenty-eight metallic mirrors in the region between wave-lengths 3800 and 1800. The most striking result of the investigation is the behaviour of silicon: it has a reflecting power of 76 per cent at λ 3000, which remains practically constant to λ 2000, but which drops rapidly to 62 per cent at λ 1870.

Nickel, stellite, and platinum come next to silicon in order of efficiency: the first reflecting about 45 per cent at λ 2000, the second and third about 35 per cent at the same point. The reflecting power of all three appears to decrease very rapidly toward the extreme ultra-violet.

The results for speculum are curious: a fresh surface gave about 22 per cent at λ 2000, an old surface hardly 8 per cent, even after it had been cleaned with chalk and alcohol; yet it is with a grating ruled on speculum that the spectrum has been extended to the very shortest wave-lengths.

[1] "Ann. d. Phy.," 81, p. 906, 1926.
[2] "Astrophysical J.," 42, p. 205, 1915.

PART II.

CHAPTER I.

APPARATUS AND METHODS.

The extreme ultra-violet may be defined as that part of the spectrum lying between wave-length 2000 and wave-length 150; the region between the latter limit and 10 Å. being described as belonging to soft X-rays. This definition may seem somewhat arbitrary, but it will serve the purposes of the present work.

Schumann, with his prism spectroscope, investigated the first 800 units of this region; the author, with a grating, extended the spectrum to the neighbourhood of 500 Å.; Millikan pushed his work to 140 Å., or even a little beyond. In considering the relative extent of the contributions of these three investigators it is illuminating to express the additions which they have made to the spectrum in a unit which for many purposes is more fundamental to the theory of spectroscopy than the wave-length, namely the frequency. If this be done it will appear that the region added by Millikan is much superior in extent to that contributed by either of the other two observers. It must also be said that Millikan has utilized his observations in the domain of short wave-lengths to better purpose than has any other single worker in this field.

Much of our knowledge of the extreme ultra-violet is due, therefore, to investigations of comparatively recent date; yet it is to the pioneer who led the way into the undiscovered country that we owe our first knowledge of the paths which must be followed in its exploration. We cannot do better than to begin by giving some account of Schumann and his labours.

Victor Schumann was born near Leipzig in the year 1841. He received his early education at Leipzig; from 1860 to 1864 he was at the Gewerbeschule at Chemnitz. It must have been during this period that he acquired that extraordinary mechanical technique which characterized all his scientific work. For a time he was employed as a designer, later he was engaged in the manufacture of machinery for the book industry; finally, he became a partner in a machine business in which he remained actively engaged until 1892, and by means of which he was able to accumulate the funds which he later spent in scientific work.

He was more than forty years of age before he was able to turn from his business to scientific pursuits. Even then his investigations were conducted in the evening or at such odd moments as he could spare from his regular profession. Photography first attracted him; one of his earliest papers, published in 1885, is on the sensitization of photographic plates. Almost immediately after this, however, he took up the pursuit of spectrum analysis, to which he devoted himself for the remainder of his active life. His first paper on the spectrum of hydrogen and upon the effect of the presence of impurities on the spectrum of mercury appeared in 1886. He must have been inspired by the idea of penetrating into the region of the extreme ultra-violet at the very beginning of his scientific studies, for it was but four years later that the article which marks the beginning of his attack on the region of the most refrangible rays appeared.

Guided by the work of Stokes, Soret, and Miller he began by instituting a very careful comparison of the relative advantages of fluorite and quartz, and becoming convinced of the superiority of fluorite as a transparent medium for rays of the shortest wave-length, he employed this substance for his prisms and lenses. Thus equipped, he followed the spark spectra of more than twenty metals to the region of λ 1820 Ångström units. He next set himself the problem of determining the factors which caused the common limit in the spectrum of so many substances. His knowledge of photographic phenomena led him to recognize the part played by

the absorption of gelatine, while his familiarity with the work of Cornu drew his attention to the absorption of the air. He put these ideas to the test by the construction of a vacuum spectroscope and by the use of special photographic plates whose emulsion was nearly free from gelatine. His efforts were almost immediately crowned with success, for a very considerable extension of the spectrum followed the use of the new apparatus. Brief accounts of this work appeared between 1890 and 1893, while a more detailed description of these researches was published in the Proceedings of the Vienna Academy in the latter year. It was during this period that Schumann gave up his business interests to devote himself entirely to his spectroscope. During the next ten years he went steadily forward, accurately and surely adding one improvement to his method after another, as the results of experiments showed the way, until he finally arrived at the limit of the spectrum set by the absorption of fluorite, near λ 1200 Ångström units.

But as early as 1897 his health began to give way. Never of a robust constitution, he had submitted to considerable privations in early life in order to obtain the funds for the purchase of books. He undoubtedly still further undermined his health by the arduous labours entailed in the construction of his apparatus. In 1903 he was forced to give up nearly all experimental work. He died on 1 September, 1913. A complete list of his papers is given in Appendix I.

Apparatus.

A detailed description of Schumann's vacuum spectroscope, illustrated by excellent drawings, is to be found in the Smithsonian Contribution, No. 1413, and a somewhat shorter account is contained in Baly's "Spectroscopy," 3rd ed., Vol. I., p. 264. To repeat in full what is readily accessible in print seems superfluous; a statement of the chief features involved in the instrument will be sufficient for the purpose in hand. Schumann's apparatus [1] consisted of a prism spectro-

[1] "Ber. Akad. Wien.," 102, II*a*, p. 625, 1893.

scope of the usual form, enclosed in an airtight casing of such ingenuity of design and perfection of workmanship that the necessary optical and mechanical adjustments could all be carried on without admitting air to the apparatus. The manipulations necessary to bring an ordinary quartz spectroscope into adjustment for the ultra-violet are sufficiently tedious, but the rapid rise of the index of refraction of fluorite with decrease in wave-length makes such work increasingly difficult after the region of the most refrangible rays is reached. The following considerations will make this clear: In order to cover the extent of the spectrum with which Schumann was concerned, nine distinct photographic fields were ultimately necessary; to secure perfect definition in any one of these fields at least eight independent adjustments were required. The only test for the accuracy of any one of these eight adjustments was by means of the photographic plate. It is obvious, therefore, that before even a single photographic field could be brought to perfect definition, a great many spectrograms had to be taken. The delay of admitting the air and repumping the apparatus after each of these spectrograms would have been intolerable. It was for this reason that Schumann faced and solved the mechanical difficulties involved in making his adjustments without admitting air to the spectroscope.

The original instrument was not large: the two fluorite lenses were of 120 mm. focal length for sodium light, and only 18 mm. aperture; the fluorite prism had an angle of 60°, the distance between the slit and the centre of the photographic plate was of the order of 32·0 cm. The angle between the optic axis of the camera lens and the photographic plate varied from 68° to 55°, depending on the part of the spectrum under investigation. For the other dimensions of the spectrometer the reader is referred to the original drawing in the Ber. of the Vienna Acad., Vol. 102, *2a*, 1893, page 694. The plates in the Smithsonian Contributions do not quite agree with the original in scale.

The dispersion of the instrument was such that the aluminium lines λ 1989·9 and λ 1854·09 were separated by

5·8 mm. when they fell at the middle of the plate; the focal length in vacuum of the lenses was for this region 106·7 mm. At the most refrangible end of the region the dispersion was, of course, much greater and the focal length correspondingly shorter.

The excellence of the slit contributed more than any other single factor to the wonderful definition obtained with the spectroscope. The slit widths employed when the finest results were secured varied from ·0075 mm. to ·0013 mm.; the time of exposure varied from a few seconds to four minutes.

For the study of the hydrogen spectrum, a discharge tube of the "end on" type communicated directly with the spectroscope, being attached to the casing which protected the slit; the discharge tube was then filled through the spectroscope with hydrogen to a pressure of about 2 or 3 mm. of mercury. When the emission of other gases was under consideration, the discharge tube was separated from the rest of the apparatus by a window of fluorite and was separately filled with the gas in question. Under these circumstances, the pressure in the spectroscope was usually about $\frac{1}{2}$ mm.

For examining the relation between the length of a column of gas and the absorption which it produced, Schumann designed a metal cell bounded by fluorite plates so perfectly constructed that the length of the gas layer could be varied continuously from 0 to 15 mm. In order to secure satisfactory operation, it was found necessary to keep the temperature constant, the device was accordingly surrounded by a water-bath. For these absorption experiments, the "end on" tube, filled with hydrogen and closed by a fluorite window, was employed as source.

The firm of R. Feuss of Steglitz have constructed a spectrograph on nearly the same plan as the original Schumann instrument, but of about twice the linear dimensions. This apparatus was employed by Handke [1] in his study of the spark spectrum of metals. Wolff [2] has used a similar instrument

[1] "Inaug. Dis.," Berlin, 1909.
[2] "Ann. d. Phy.," 42, p. 825, 1913.

constructed by Feuss with lenses of 15 cm. focal distance and 1·6 cm. aperture.

Trowbridge [1] has described a vacuum prism spectrograph of an entirely different type, in which the lenses were replaced by mirrors. Up to the present time, however, this instrument has not been tested in the region of extremely short wave-lengths.

More recently L. and E. Bloch [2] have used prism instruments of special design.

While a prism spectroscope is admirably suited for general exploration in the Schumann region because of its compact form and the brilliancy of its spectrum, it is unfitted for wave-length determinations unless the dispersion curve for the prism is known. Several attempts were therefore made to devise a grating instrument with which wave-length measurements could be carried out. The first of these attempts was not crowned with much success. Morris Airey [3] worked with a transmission grating on fluorite and with a concave grating. He measured a few lines in the spark spectrum of aluminium. The values are reprinted in Watts' Tables; they do not agree with the measurements of other observers. Wolff [4] tried to use the fluorite transmission apparatus but abandoned it for the prism form. Kayser and Runge [5] designed two reflection grating spectrographs to be used in vacuum, but they did not employ them beyond the region of λ 1850.

Besides the fundamental advantage of a concave grating over a prism system, the former is much more easily adjusted than the latter, for, by properly proportioning the apparatus, the whole Schumann region may be obtained in good focus on one photographic plate at one time. On the other hand, the distribution of the light in the spectra of various orders usually makes the intensity of the light in any one grating spectrum inferior to that obtained with a prism. Finally, the

[1] "Zeitsch. f. Instrumentenkunde," 30, p. 334, 1910.
[2] "Journal d. Phy.," 2, p. 229, 1921.
[3] "Memoirs Manchester Phil. Soc.," 49, III., p. 1, 1904.
[4] "Ann. d. Phy.," 42, p. 825, 1913.
[5] "Abh. Berlin Akad.," III, p. 5, 1892.

great optical distance between slit and photographic plate necessitates very great freedom from leak in the grating spectroscope.

The first successful attempt at wave-length measurement in the Schumann region was carried out at Harvard University with a concave grating.[1]

The Grating Spectroscope.

The original vacuum grating spectroscope is now chiefly of historic interest, for considerable improvements have been made in the design of such instruments during the past fifteen years. The remainder of this chapter is devoted to a discussion of the principles which should govern the construction of grating spectroscopes for use in the extreme ultraviolet, to the description of a few characteristic types, and to some questions of technique.

Vacuum grating spectroscopes may be divided into two classes: in the first, the light falls nearly normally on the grating, in the second, grazing incidence is employed. The great majority of instruments in use at the present time belong to the first type, but the second presents most interesting possibilities.

There is one factor at least which may be said to effect the efficiency of both kinds of instruments, and that is the perfection of the vacuum. In Schumann's day, and for some time after, it was the custom to wash the body of the spectroscope with hydrogen and to work with an atmosphere of the gas at about a millimetre in the instrument. This practice is now known to be distinctly harmful. Not only are the shortest wave-lengths absorbed by the hydrogen, but the products of the ionization of the gas [2] reduce the effective life of the grating through tarnish, and fog the photographic plate. The body of the vacuum spectroscope should be maintained at the best possible vacuum; this is the first and perhaps the most important rule applicable to vacuum spectroscopy in

[1] "Astrophysical J.," 23, p. 181, 1906.
[2] K. Cole, "Phy. Rev.," 28, p. 781, 1926.

general. As a corollary it is evident that water vapour and the vapours of organic substances such as grease and wax must be excluded.

In all work where the whole extent of the extreme ultra-violet is to be investigated, the use of a window between the source and the slit is out of the question. In order therefore to preserve a high vacuum in the body of the apparatus, a special arrangement of pumps is necessary whereby the gases from the neighbourhood of the source are removed at a point close to the slit itself. This is of fundamental importance.

A second important matter is the relative position of the source of light and the slit: obviously the distance between the two should be made as short as possible, always bearing in mind the possibility of danger to the latter from heat or bombardment from the source. In many spectrographs where Rowland's arrangement is employed, grating, slit, and photographic plate being all on the great circle whose diameter is the grating's radius of curvature, it is mechanically impossible to place the slit and photographic plate inside the body of the vacuum receiver without introducing too great a distance between the slit and the light source. This difficulty, and one of the ways in which it can be overcome, will be better understood when we come to the description of the particular type of instrument in use at Harvard.

There is a third subject of general interest which may be put in the form of a question: Is it worth while to make elaborate provision for the introduction of the photographic plate into the body of the spectroscope through some sort of air lock, to the end that the vacuum in the main body of the apparatus may be preserved? The time saved in pumping is a thing of secondary importance; but the possibility of reduction in the amount of gases which cling to the inside of the apparatus is well worth considering. Such a reduction will be the more likely if the receiver remains evacuated over a considerable period. On the other hand, ingenious air locks mean movable joints and connexions, their presence increases the chance of introducing absorbing vapours into the spectroscope. As a result of considerable experience, the author is

prejudiced in favour of simplicity of construction, especially in those cases where light of the very shortest wave-length is to be investigated.

The designs of most of the instruments where nearly normal incidence is used have much in common. The concave grating, usually of about a metre radius, is placed at the end of a tube, in a suitable holder; the other end of this container carries the slit and the photographic plate. This tubular receiver is closed by plates or conical joints made airtight with rubber gaskets or wax. One design differs from another in the relative positions of photographic plate and slit, in the means of making the necessary adjustments, and in the manner of closing the openings in the receiver. The material employed is usually brass; if castings are used, they must obviously be of a very homogeneous character. It does not seem desirable to describe all the various instruments now in use, but the following rather detailed account of the vacuum spectrograph at present employed at Harvard University may be of interest as illustrating one way in which the various problems of design may be met.

The end of the apparatus which contains the grating need not particularly concern us; it is closed by a vertical brass plate made airtight by a thin ring of soft wax. Most of the adjustments for focus are made by removing this plate and manipulating the grating.

The arrangement of the slit and the plate-holder end of the instrument presents some novelties of design which are illustrated in the drawing of a horizontal section (Fig. 2).

The body of the spectroscope consists of a drawn brass tube of 14·9 cm. internal diameter, which carries at the grating end a flange and to which, at the other extremity, is permanently soldered the plate A. This plate carries the slit tube B, and from it protrudes the rectangular brass box C, 14 cm. long, 7·8 cm. high, and 5·5 cm. wide. The brass plate D, upon which the plate-holder is mounted, slips into this box and rests upon its floor; a spring G, pressing on the back of the box, holds the base plate in position. The opening at the end of C is surrounded by a flange, and is closed by a plate E,

the joint being made airtight by a ring of soft wax. To facilitate adjustment there is a slot in the back of C covered with a glass plate W. This window is made light-tight by a cap.

The plate-holder slides in vertical ways on the back of the

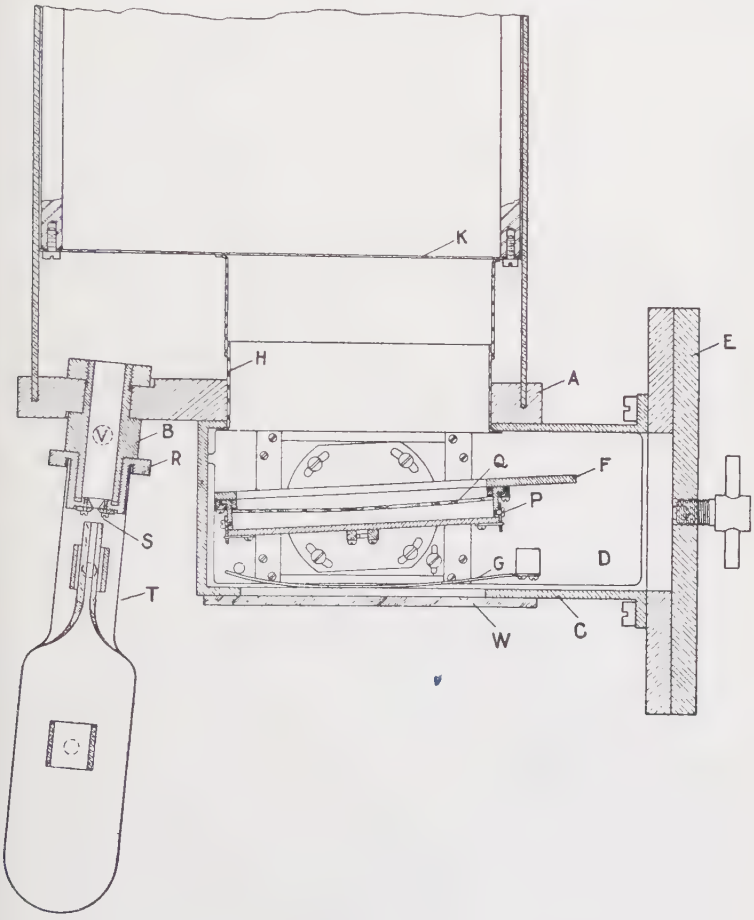

FIG. 2.

vertical plate F; this plate is so mounted that it may be turned about a vertical axis, and it is also capable of motion in a direction toward the grating or away from it. These arrangements are designed to facilitate the last stages of the focusing operations.

The photographic plate is 8 cm. long and $2\frac{1}{2}$ cm. wide. A device, very similar in principle to the arrangement used in my earliest spectroscope, is operated by an electro-magnet just above C; by its means the plate-holder may be allowed to fall under gravity in its ways by successive equal steps; thus a number of exposures may be made on the same photographic plate.

The arrangements of the diaphragms in a spectroscope of this kind are of considerable importance. Light from the grating reaches the photographic plate through a slot 2 mm. wide and 7·8 cm. long in F. There is a corresponding slot in the plate A, which is furnished in turn with a narrow, rectangular box-like sleeve H, which makes connexion through a second similar sleeve with a system of diaphragms K, extending the length of the instrument (Fig. 3).

The slit S has a height of 0·16 mm.; its width is usually about 0·04 mm. It can be removed from the tube B for the purpose of adjustment by melting the Khotinski cement which is employed to render the joint between B and the collar R, on which the slit is mounted, airtight. The discharge tube T is fastened to R with cement. When the spark or arc discharge is employed, a suitable container is substituted for this tube, the maximum diameter of this vessel being obviously determined by the distance between the slit and the brass box C. The arrangement of the pumping system is important; the outlet tube V is destined to remove the gas which comes through the slit from the discharge tube. The body of the spectroscope is exhausted by means of two tubes, about 1·4 cm. diameter, placed symmetrically with respect to the middle point of the instrument.

The exhaustion is effected by a mercury diffusion pump, or by the Holweck [1] rotary pump, backed by the Trimount vacuum pump, which I have long employed; a liquid-air trap and two drying tubes are placed between the pumping system and the spectroscope.

The success of this type of instrument depends chiefly on

[1] "Comptes Rendus," 177, p. 43, 1923.

the small dimensions of the slit and on the arrangement of vacuum pumps whereby the body of the spectroscope is kept at a good vacuum while a pressure of several millimetres of mercury may be maintained in the vessel containing the discharge. So much, then, for this particular spectroscope.

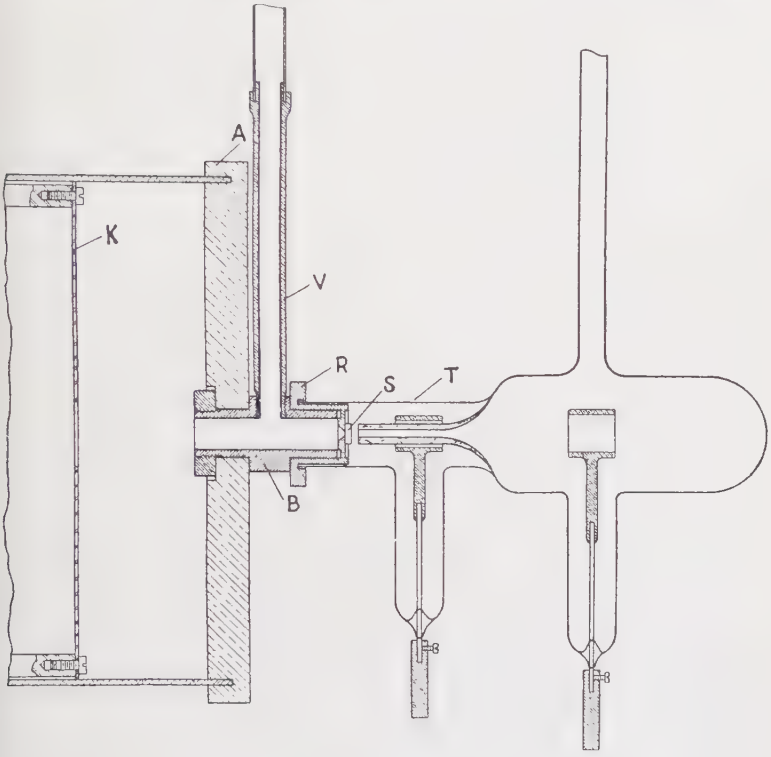

FIG. 3.

Of the instruments used by the ever-increasing number of investigators in this field, the following deserve mention :—

Millikan,[1] who has been chiefly interested in the radiations from one particular source, has placed his vacuum spark within the body of the receiver.

Hopfield,[2] in some of his work, has broken away from the canonical tubular form of the receiver, and has substituted a

[1] Sawyer, " Astrophysical J.," 52, p. 286, 1920.
[2] " Phy. Rev.," 20, p. 573, 1922.

sector-shaped cast brass, holding at the smaller end a concave grating of 50 cm. radius of curvature.

McLennan [1] and his students have used a spectrograph in which the grating rests on its side with its rulings horizontal, thus producing a vertical spectrum. The slit is not in the plane containing the medial line of the spectrum and the centre of the grating, but is placed at one side, in a second plane at right angles to that just mentioned, and passing through the centre of the photographic plate. This departure from the usual arrangement is said to possess some advantages. Furthermore, the openings in the vacuum receiver are closed by cones having their axes vertical.

The instrument due to Lang [2] resembles that of McLennan, but it contains several improvements. The light source is brought into close proximity to the slit, and an ingenious device permits the photographic plate to be introduced into the receiver through an air lock. It is also noteworthy as illustrating an attempt to secure greater dispersion by the use of a grating of nearly 2 metres' radius. The receiver has a capacity of about 70 litres; that the evacuation of this considerable volume presents no great difficulty is a fact which bears testimony to the efficiency of the modern vacuum pumps.

As has been already remarked, the writer's experience during the last quarter of a century has prejudiced him in favour of simplicity of construction; in spite of this fact, he has noted with much interest the complicated design of an instrument described by Bloch,[3] in which all adjustments are made without the necessity of admitting air into the receiver.

Sources.

There are four types of light source which have proved useful in the extreme ultra-violet: the high vacuum spark, the spark operating in an atmosphere of transparent gas, the

[1] "Proc. Roy. Soc. Lond.," 98, p. 114, 1920.
[2] "Journal Optical Soc. Am.," 12, p. 523, 1926.
[3] "Revue d'Optique," 5, p. 63, 1926.

arc, and the discharge tube. The first, often called the hot spark, was originally described by Wood; it was rediscovered by Millikan, who used it not only to extend the spectrum to the extreme limit of about 140 Å., but also to carry on a long series of brilliant theoretical and practical investigations in the extreme ultra-violet. In this device the terminals are placed in the highest possible vacuum available under the circumstances; they are very close together, being separated by a distance of a millimetre or less. A disruptive discharge is applied, either directly or through an external gap placed in series. The value of the capacity and of the other electric constants are chosen in such a way as to produce a surge of maximum intensity. A key operated either automatically or by hand is often placed in the primary of the transformer, for the purpose of interrupting the discharge from time to time; this step is necessary as a precaution against the harmful evolution of gas due to the over-heating of the electrodes.

This high vacuum spark is not only very rich in light at the extremity of the optical spectrum, but it also often gives out X-rays of sufficient intensity to reveal the bones of the hand placed half a metre from it.

This type of source, in spite of its almost unique advantages, has some serious drawbacks. The electrodes are eaten away by the discharge with considerable rapidity, even when the material of which they are formed is of a refractory substance, such as tungsten. The products of this disintegration are blown with violence against the sides of the vessel which contains the spark, into the jaws of the slit, and even in extreme cases against the surface of the grating itself. As a result the containing vessel becomes liable to puncture through the formation of a conducting layer, the slit, especially if fine, is likely to become plugged, and the surface of the grating may be subject to permanent injury. Moreover, the burning away of the electrodes renders the position of the spark uncertain, and thus ruins the constancy of the source.

A numerical example may be of some interest in this connexion. The author usually employs an alternating current transformer, operating on a 110-volt 60-cycle circuit, and taking

about 10 amperes in the primary, with a voltage of perhaps 20,000 volts in the secondary, as estimated by spark length between needle points. This transformer is connected to a condenser formed of "Navy Jars," having a capacity of ·004 microfarads. This condenser is connected directly to the vacuum spark gap, which, in turn, is placed within a distance of $2\frac{1}{2}$ cm. from the slit. With this arrangement, and with the Harvard vacuum spectrograph just described having a slit width of ·03 mm., it is possible to obtain a record of lines in the spectrum of copper at, or near, wave-length 200 Å., with an exposure of 500 one-second flashes, each separated by an interval of one second.

The spark or the arc which is to be operated in an atmosphere of transparent gas is enclosed in a vessel of pyrex glass, or of quartz, very similar in general design to that employed with the hot spark, but provided with means of admitting a current of gas under reduced pressure. There are various means of imparting the necessary motion to the electrodes; the author employs a screw of 48-to-the-inch pitch, very accurately cut in brass and working in a nut of the same material $2\frac{1}{8}$ inches long. A little stop-cock grease applied to the upper half of the thread makes the joint perfectly air-tight. This device is also used successfully with the hot spark where the best possible vacuum is necessary. The gas and the pressure under which it is to be used depend on the part of the spectrum under investigation. Hydrogen, helium, and nitrogen may all be employed in a manner which will be better understood when the transparencies of these substances is under discussion; the pressure may be a few millimetres. In the case of the spark, if the gas pressure is low, it will be necessary to employ an external spark gap in series to secure the desired brightness.

In the best practice the only communication between the spark or arc chamber and the body of the spectroscope is the short and narrow slit. The chamber is provided with a separate connexion with the vacuum pump, which may be closed by a suitable stop cock; the gas which flows continuously into the chamber in the neighbourhood of the discharge is

removed on the grating side of the slit by a special pump connexion. The simplest manner of regulating the flow of the incoming gas is by means of a long capillary tube. Hopfield [1] has invented an ingenious variation on this method.

Most discharge tubes designed for spectroscopic work contain a constriction in which the electric current is concentrated, and where the brightness is at a maximum. For work in the extreme ultra-violet it is specially important that this constriction be placed as near the slit as possible, both for the sake of illumination and for the purpose of making absorption of light by the gas in which the discharge takes place as small as possible. One way of accomplishing these results is by using an internal capillary; the type which has long been employed by the author is illustrated in Fig. 4, the relative proportions are shown by the scale.

By this device the end of the capillary may be brought to about 1 centimetre of the slit. The tube is usually of pyrex glass or of quartz, the electrodes may be of any of the materials commonly employed, such as aluminium, or, preferably, tungsten. As an example of the intensity of this source toward the extreme limit of the ultra-violet, it may be stated that, when the spectrum of helium was under investigation in the region between 400 and 500 Å. an exposure of an hour was necessary, with a direct current of 15 to 20 ma. In this connexion it is well to note that when a continuous current is employed, the polarity of the tube has some effect on the result; it seems probable that it is advantageous to make the electrode nearer the slit negative.

The author has obtained lines of nearly the shortest wave-length which have ever come under his observation by the use of a strong disruptive discharge and an internal capillary tube, the radiation in question, which lies at 165 Å., being presumably due to the material of which the capillary is composed. It is therefore not true, as has sometimes been stated, that the vacuum spark is the only source from which optical radiation of the very shortest wave-length can be procured.

[1] "Journal Optical Soc. Am.," 12, p. 391, 1926.

The necessity of maintaining the best possible vacuum in the body of the spectroscope has been emphasized; but under some experimental conditions it is impossible to avoid a certain amount of gas in the main part of the instrument. Under these circumstances, it is very desirable to reduce the

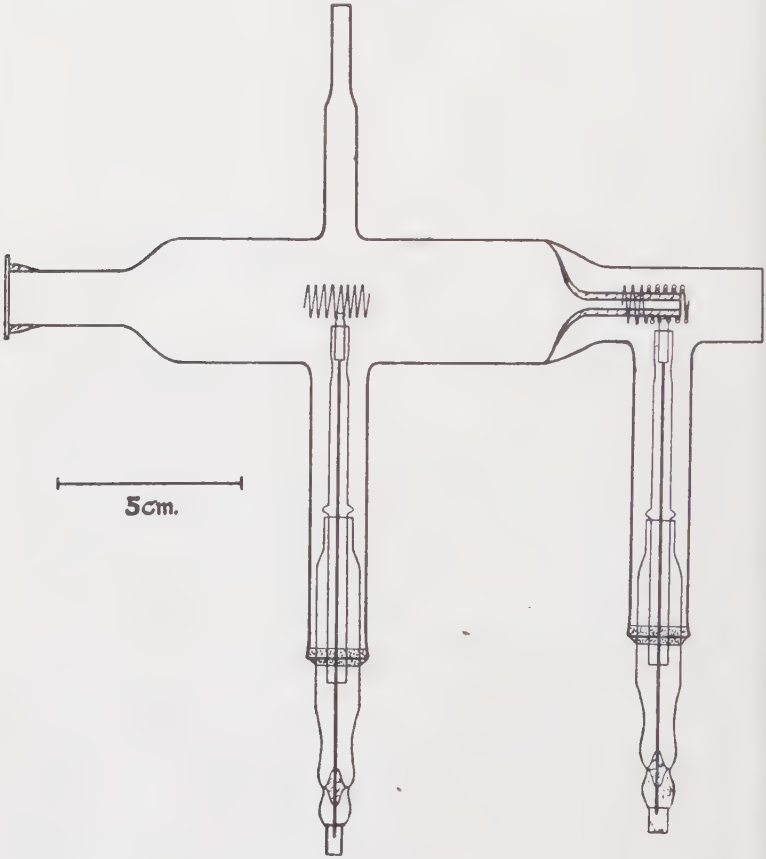

Fig. 4.

time of exposure to a minimum, to the end that the gas may remain in contact with the photographic plate and with the grating surface for as short a period as possible. Hopfield [1] has accomplished this result by using very heavy currents in a discharge tube provided with a cooling jacket and a circula-

[1] "Phy. Rev.," 20, p. 577, 1922.

tion of oil. The tube has a power capacity of 2·25 kw., and carries a current of 300 milliamperes or more; by its use the time of exposure is reduced to a few minutes.

The Continuous Spectrum.

For the study of absorption the production of a continuous spectrum in the extreme ultra-violet is of great importance. Schumann has mentioned radiation of this type in hydrogen extending below 2000 Å.; Lewis [1] has confirmed these results, and has shown that the spectrum reaches to the neighbourhood of 1600 Å.; Leifson,[2] using a long discharge tube without a constriction, through which a current of hydrogen was maintained, has utilized the resulting continuous background. Unfortunately, the continuous hydrogen spectrum covers but a small part of the extreme ultra-violet. Recently the author [3] has shown how continuous radiation may be produced, extending as far as 900 Å. The procedure consists in charging a condenser of about one-half microfarad capacity with a direct current, and then discharging it through a vacuum tube of the internal capillary type, arranged in series with a half-centimetre spark gap. The best results are obtained with a discharge tube of common glass; it is important that the capillary be not too large—a diameter of about 1 mm. is satisfactory. The material of the electrodes is not important; tungsten is often employed. The continuous spectrum seems to owe its existence to the disintegration products of the glass set free by the erosive action of the discharge; its strength depends hardly at all on the nature of the gas in the discharge tube. The experiment is not without mechanical difficulties, for the slit of the spectroscope frequently becomes plugged up by glass dust, the removal of which involves a troublesome process.

Absorption.

In the study of the absorption of solids, the materials under investigation may be introduced in front of the slit of a

[1] "Science," 41, p. 947, 1915. [2] "Astrophysical J.," 63, p. 73, 1926.
[3] "Science," 64, p. 89, 1926.

vacuum grating spectroscope by some mechanical device, care being taken to employ a source which will not spatter the specimen.

Some time ago the author [1] employed a special form of apparatus by the use of which he was able to test the transparency of a number of substances with rapidity. In this instrument the spectrum was formed by a fluorite prism and a concave speculum mirror; no slit was used, the source being the open end of a capillary tube, the materials under investigation were mounted over holes in a disc, and were interposed in turn between the source and the prism. A fluorescent screen or a Schumann photographic plate served as a detector, the opacity of the fluorite prism set the limit of the spectrum at about 1300 Å. Experience showed that this rough instrument could be trusted to detect the difference in transparency of two substances the length of whose spectra, when obtained with a grating, differed by not more than 15 Å. units.

There are two methods which may be employed in testing the transparency of gases. In the first, a cell closed at each end by fluorite windows is placed in front of the slit; in the second, the gas is admitted directly into the body of the spectroscope. In the first, the region which may be studied is obviously limited by the transparency of the fluorite; in the second, the grating may well run some risk of injury from the gas. In his early investigations the author employed both methods. Much more recently Leifson [2] has made use of the fluorite cell, and Hopfield [3] has admitted the absorbing gas into the body of his spectroscope.

Gratings.

The gratings which have been employed in the investigation of the extreme ultra-violet are the product of the following ruling engines: The Blaesthwood machine at the National Research Laboratories in England; Professor Michelson's

[1] " Astrophysical J.," 25, p. 45, 1907.
[2] *Ibid.*, 63, p. 73, 1926.
[3] " Phy. Rev.," 20, p. 578, 1922.

machine at the University of Chicago; the machine at Mount Wilson Observatory at Pasadena, California; and last, but by no means least, the Rowland engines at Johns Hopkins University.

The radius of curvature is usually about a metre, though 50 cm. gratings are not uncommon, and the author has even worked with a pigmy instrument of 25 cm. radius. As has already been mentioned, some investigators are now employing gratings of 2 metres' radius, with the purpose of obtaining larger dispersion. The ruling is usually about 15,000 lines to the inch, though 30,000 lines have been used.

It seems to be universally conceded that a light ruling is essential for success in the extreme ultra-violet, especially if the limit of the region is to be reached.

The material on which the grating is ruled is of great interest and importance. Speculum has been generally employed, and it was with a grating on this alloy that Millikan succeeded in extending the spectrum to its present limit near 140 Å. This result is all the more remarkable when we remember the very low reflecting power of speculum in the region between 2000 and 1800 Å., as determined by Hulburt.

Recently Wood has succeeded in producing a satisfactory grating very lightly ruled on glass. A test by the author [1] revealed the considerable superiority of this instrument over a speculum grating. Both gratings produced spectra extending to near 200 Å., but the spectrum from glass was much the stronger of the two, especially in the region on the short-wave side of 500 Å. It must be noted, however, that, though the speculum grating in question had been under observation for more than eighteen months without showing any marked falling-off in the intensity of the extreme ultra-violet spectra it produced, yet the instrument could not be said to possess a fresh surface. It may be regarded as an open question whether the glass grating is superior in performance to the original, freshly ruled instruments used by Millikan.

It is important to note that Thibaud has confirmed the

[1] Lyman and Wood, "Phil. Mag.," 2, p. 310, 1926.

observation on the superiority of glass over speculum for a grating at tangential incidence.

One thing can be stated with tolerable certainty : if proper precautions are taken, the surface of the glass grating is less liable to change than that of a grating ruled on speculum. This is important, for tarnish is a great enemy of progress in the extreme ultra-violet. It must be admitted, however, in this connexion, that a film of grease will injure the performance of a glass surface. This is illustrated by the fact that the instrument just mentioned was observed to lose part of the efficiency after some months' use ; on removal from the spectroscope the grating appeared perfectly clean, but on washing with specially purified methylic alcohol and anhydrous ether the reflecting power was restored.

Wood has also produced a satisfactory concave grating on quartz. The author's test, however, was disappointing ; the instrument, though giving excellent definition, showed hardly any better performance than the grating on glass. The permanence of the surface, however, would be beyond question.

The author [1] has experimented with the rejuvenation of speculum gratings by spattering with various metals. Platinum was tried, at first with some success, but after a time the film seemed to lose contact with the speculum, with the result that the last state of the grating was worse than the first. Spattering with silicon has been attempted, and this produces some improvement in the reflecting power ; the process looks promising, and is well worth further investigation.

It may be remarked that the reflecting power of some of the best gratings at or below 200 Å. is capricious and unsatisfactory. The effect of tarnish is well known, but the part played by grease films has not, perhaps, been sufficiently recognised.

There is one more subject to which the reader's attention should be particularly directed. In all investigations carried on with concave diffraction gratings the results are influenced by the peculiarities of these instruments. It cannot be too strongly emphasized that in the examination of an unknown

[1] " Astrophysical J.," 60, p. 11, 1924.

spectral region the reality of all the lines obtained with any one grating cannot be assumed; the ghosts,[1] or false spectra, which occur in even the best instruments being a source of error which cannot be neglected. It is extremely desirable that the spectrum under consideration should be examined with several gratings ruled under different conditions and, if possible, on different engines.

Methods of Measurement.

In determining the wave-lengths of the lines in the hydrogen spectrum which served as the original standards in the Schumann region, two methods were used: The values of all the lines were first obtained by the "two-slit method"; these wave-lengths were then checked by obtaining the stronger lines in the second spectrum and comparing their positions with known iron lines in the first spectrum. The average difference between the values obtained by the two methods was 0·3 Å.

The reader is referred to the original [2] paper for an account of the two-slit method, and for a detailed description of the way in which the measurements were carried out.

In the best modern practice the line under investigation is photographed in higher orders of the spectrum, by which process its wave-length may be determined by comparison with known lines in the visible and in the ultra-violet. By this method a set of standards has been determined throughout the region of the extreme ultra-violet. In some cases, particularly in that of the atomic spectrum of hydrogen, it is possible to check these measurements by comparison with computed values based on the theory of series spectra.

In measuring plates obtained from a vacuum spectrograph it is well to remember that the spectrum is rarely normal. Methods of correction have been worked out both for flat [3] and for curved plates.[4]

[1] Runge, "Ann. d. Phy.," 71, p. 178, 1923.
[2] Lyman, "Astrophysical J.," 23, p. 202, 1906.
[3] Millikan and Bowen, "Astrophysical J.," 53, p. 150, 1921.
[4] Hutchinson, "Astrophysical J.," 58, p. 280, 1923.

When identifying lines of uncertain origin, some remarks of Bowen [1] are well worth attention; they are in substance as follows: Many elements have such weak lines in the visible that they are not usually thought of as sources of radiation in the ordinary part of the spectrum, yet they possess very strong spectra in the extreme ultra-violet, and their presence must be carefully watched for. This is particularly true of the carbon, nitrogen, oxygen, fluorine families. It is often advantageous to take the spectrum on the less refrangible side of 2000 Å. by means of a separate quartz or glass spectrograph at the same time the exposure with the vacuum spectrograph is made, as a further aid in the identification of impurities.

Grating at Tangential Incidence.

A. H. Compton [2] has used a plane grating at tangential incidence for the diffraction of X-rays; Thibaud [3] has carried out experiments of the same character but of an improved form; he has also devised an instrument for work in the extreme ultra-violet. The description which follows is taken from Thibaud's paper.

Following the elementary theory, a plane grating of constant d (distance of two contiguous elements of the apparatus), illuminated by a monochromatic pencil of wave-length λ, making an angle θ with its surface, produces on either side of the reflected ray diffracted rays, the nth order of wave-length λ appearing at an angle $(\alpha + \theta)$, such that

$$n\lambda = d[\cos\theta - \cos(\alpha + \theta)].$$

This relation may be written, when θ is very small,

$$n\lambda = \frac{d}{2}(\alpha^2 + 2\alpha\theta) \quad \text{or} \quad n\lambda = \frac{d}{2}\Delta\alpha.$$

Such are the equations which determine the dispersion of a grating used at tangential incidence.

[1] "Journal Optical Soc. Am.," 13, p. 93, 1926.
[2] "Proc. Nat. Acad. Sci.," 11, p. 598, 1925.
[3] "Journal d. Phy.," 8, p. 13, 1927.

If one compares this method of using a grating with that commonly employed where the illumination falls normally on the surface, one observes that tangential illumination possesses the inconvenience of producing a spectrum which is not "normal," but in which the dispersion decreases progressively toward the longer wave-lengths. On the other hand, it possesses a very great advantage from the point of view of dispersive power in the extreme ultra-violet. Consider two identical gratings, the one illuminated by a pencil normal to the surface, the other by a pencil which is exactly tangent. They will diffract the same wave-length λ through the angles

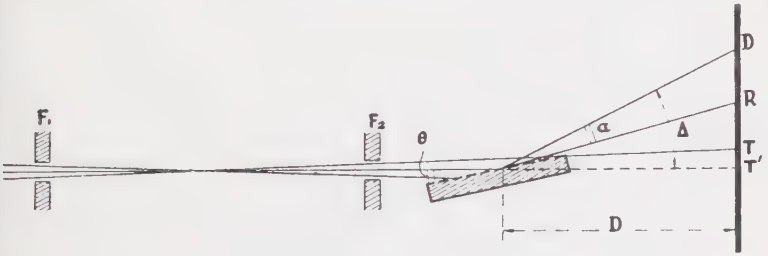

FIG. 5.

α_1 and α_2 respectively, which may be written, if the angles are small, and if we are dealing with the first order spectrum,

$$\alpha_1 = \frac{\lambda}{d} \quad : \quad \alpha_2 = \sqrt{\frac{2\lambda}{d}},$$

thus the dispersions for the same wave-length λ will be for one and for the other mode of illumination,

$$p_1 = \frac{d\alpha_1}{d\lambda} = \frac{1}{d} \quad \text{and} \quad \frac{d\alpha_2}{d\lambda} = \frac{1}{\sqrt{2\lambda d}},$$

respectively, the last expression being a function of the wave-length. The dispersion produced by a grating with tangential incidence exceeds considerably that of a grating with normal incidence for light of very short wave-length; thus for the radiation $\lambda = 1860$ of the ultra-violet spectrum of aluminium, a grating of 200 lines illuminated tangentially gives the same dispersion as a grating of 730 lines illuminated normally; and for a radiation $\lambda = 500$ Å., a grating of 570 lines used

tangentially will give the same dispersion as one of 2400 lines used normally.

Another question which must be faced in considering the new method is that of the good definition of spectral images. Can the plane grating alone furnish narrow rays? It is necessary in the ordinary apparatus to employ either a lens after the plane grating, or a concave grating, to form the image of the spectrum, the method of diffraction at grazing incidence is very favourable from this point of view. Let i be the angle which the diffracted beam of wave-length λ makes with the plane of the grating, then

$$i = \theta + \alpha = \sqrt{\frac{2n\lambda}{d} + \theta^2}.$$

Differentiating with respect to θ,

$$\frac{di}{d\theta} = \frac{\theta}{\sqrt{\frac{2n\lambda}{d} + \theta^2}},$$

an expression which is sensibly zero, since θ^2 is small compared to $\frac{2n\lambda}{d}$. The angle of diffraction i remains constant, therefore, as the angle θ undergoes slight changes, such as occur when the grating is illuminated by a slightly diverging beam. Thus the following theorem results: In the use of a grating with tangential incidence each diffracted monochromatic beam forms a parallel pencil, even if the incident beam is slightly divergent. If only rays for which the angle of diffraction α remains small are used, the beams will be extremely narrow, and one would expect to obtain fine spectral lines on the plate, no matter what distance separates the plate from the grating. So much, then, for this theory.[1]

The vacuum spectroscope of Thibaud is simple and compact; it consists of a brass tube 40 cm. long and 15 cm. diameter, closed at each extremity by a thick bronze disc bearing on a flange made tight with rubber grease. Of these

[1] See also Morris-Airey, "Phil. Mag.," 11, p. 414, 1906; Porter, *ibid.*, 15, p. 762, 1908, and 5, p. 1067, 1928.

discs one, pierced at its centre by a hole, carries all the spectrographic arrangements: on the one side the spark chamber, on the other the two collimator slits and the grating mounting; the assembly of the parts and their adjustment is thus facilitated. The light passes from the vacuum spark, through the two slits in succession, falls on the grating at grazing incidence, and is finally received by the photographic plate. The distance from grating to photographic plate is extremely short, being from 9·8 cm. to 13·4 cm.; the distance of the source to the grating appears to be of the order of 16 cm. For details of construction and of the arranging of the pumping system the reader is referred to the original article.

Thibaud has obtained his best results with a grating ruled on glass with 200 lines to the millimetre. He has also tried a Rowland grating on speculum of 568 lines to the millimetre (14,436 to the inch), but with much less favourable results, the spectra from the second instrument being far inferior in intensity to those obtained with the first, in the region of the shortest wave-lengths.

The copper high-vacuum spark has been used as source, permitting a comparison with the wave-length measurement of Millikan; the agreement between 892 Å. and 164 Å. is satisfactory.

It is interesting to note that, owing to the non-linear character of the spectrum, the whole range between the visible at 6000 Å. and 140 Å. is registered on one and the same photographic plate.

The advantages of the vacuum tangential grating spectroscope are three in number: First, its compact form, by which a short light path is secured; second, the intensity of the spectra which it produces; and third, the high dispersion which it yields in the extreme ultra-violet.[1]

The diffraction of X-rays is a subject which lies outside the field covered by this book; nevertheless it seems worth while to add a few words on the theory of the plane grating

[1] See also Hoag, "Astrophysical J.," 66, p. 225, 1927.

in connexion with this phenomenon, in order to emphasise the difference in behaviour of light and X-rays as far as the use of a grating is concerned. Again we shall follow Thibaud.

The diffraction of Roentgen rays by ordinary gratings used tangentially cannot be employed practically unless the diffracted pencil possesses a sufficient intensity. However, X-rays, according to the most recent estimates, possess an index of refraction μ, very near, but slightly less than unity, such that

$$\mu = 1 - \delta, \text{ where } \delta \text{ is of the order of } 10^{-6}.$$

It follows that, if a beam of X-rays illuminates a plane reflecting surface (or a grating) tangentially, total reflection of the beam results if the angle θ is less than a certain critical angle θm given by $\theta m = \sqrt{2\delta}$, the phenomenon corresponding exactly to what is called total internal reflection in ordinary optics.

The important fact follows that, if care is taken when using a grating at grazing incidence to choose θ less than θm, total reflection will take place and a maximum intensity of the diffracted ray will result. This condition necessitates fine adjustment and a narrow beam, since the limiting angle θm never exceeds about ten minutes of arc. As has been already mentioned, it was A. H. Compton who first proposed this method, and who carried it into execution.

It is obvious that, while the advantages for optical spectra in the use of the grating at grazing incidence consist in the superior brightness and the increased dispersion, the use of the grating for X-rays depends fundamentally on total internal reflection in which the material of the grating plays the part of the lighter medium.

Preparation of the Photographic Plates.

No matter what form of vacuum spectroscope is employed, no progress can be made in the region of extremely short wave-lengths unless dry plates specially adapted to the purpose are used. The investigations of the factors which control the sensitiveness of such plates and the evolution of

the technique necessary in their manufacture, therefore, form a contribution of fundamental importance.

Soret [1] showed that gelatine absorbs strongly in the ultra-violet, and Schumann [2] extended these observations, using a series of quartz plates coated with gelatine in layers from ·13 mm. to ·00004 mm. thick. He observed that the silver bromide grains of his photographic plate varied between ·0012 mm. and ·0017 mm. in diameter, and his experiments indicated that a layer of gelatine of this order absorbed strongly near λ 2265 and increased rapidly in opacity with decreasing wave-length. On the other hand, experiments with silver bromide showed that this substance absorbed strongly in the ultra-violet. Taking this absorption as an indication of photo-chemical activity of the salt, he concluded that the lack of sensitiveness of the ordinary dry plate was not due to the lack of activity of the silver bromide but to the absorption of the gelatine contained in the emulsion. Accordingly,[3] he first tried precipitating a layer of silver bromide directly on glass, and succeeded in producing a plate far more sensitive to the extreme ultra-violet than anything which he had previously made. Unfortunately, the silver salt did not adhere firmly, and the film after development was apt to float away during the process of fixing. This action could be lessened by making the film extremely thin, but it always constituted a serious fault in the method. He next tried coating the glass with gelatine and then allowing the silver bromide to settle on this surface. This procedure was a marked improvement, the gelatine playing a double rôle: not only did it serve as a means of binding the salt to the glass, but its presence increased the photo-chemical sensitiveness of the silver bromide. Moreover, plates of this kind gave a negative showing some contrast, a property which was entirely lacking in the negatives obtained with the pure salt.

A long series of experiments convinced Schumann that

[1] "Arch. d. Sc. phy. et nat.," III, Vol. X, p. 453, 1883.

[2] "Ber. Wien. Akad.," 102, II*a*, pp. 460 and 994; "Astrophysical J.," 3, pp. 220 and 387, 1896; 4, p. 144, 1896.

[3] "Ber. Wien. Akad.," 102, II*a*, p. 994.

pure silver bromide gave better results than any combination of haloid salts, when precipitated in this way on gelatine. In addition to gelatine he tried agar-agar and gum-arabic as binding materials, but these experiments met with no success. Schumann also tried various methods of treating the finished plates. He discovered that bathing the plate in dilute ammonia increased the sensitiveness somewhat, but ultimately he found better means for securing the same end. Attempts at intensification with mercuric chloride were not successful.

He made the useful observation, however, that the size of the grain of the plate depended on the nature of the developer employed. Thus, a developer containing potassium bromide produced a coarse grain with a silver bromide plate; a developer free from potassium bromide gave a fine grain.

The process which Schumann [1] finally adopted for making his plates depended upon the same principle as the method last described, but differed in technique. In brief, it consists of forming an emulsion of silver bromide rather weak in gelatine; this is first sensitized by heating, it is then allowed to solidify, and is washed and dissolved in a great quantity of water. The diluted emulsion thus formed is poured on glass plates and allowed to settle. The superfluous fluid is then drained off and the plates dried.

The sensitiveness of the plates so prepared depends to a large degree on the temperature to which the emulsion is raised and the length of time during which it is exposed to this temperature: it is also somewhat dependent upon the temperature of the room in which the emulsion is allowed to settle. The perfection of the film as shown by its freedom from fog and streaks, as well as by its keeping quality, depends upon the purity of the solid ingredients and of the distilled water employed, a small amount of organic matter exercising a very prejudicial effect. The nature of the developer and its temperature also play an important rôle.[2]

Plates prepared in this way are extremely sensitive to the extreme ultra-violet; they also possess the rather remarkable

[1] "Ann. d. Phy.," 5, 349, 1901. [2] See Appendix.

characteristic of being quite insensitive to the light of longer wave-length than λ 3000. They are the only means at present employed for detecting light of the very shortest wave-length.

Some attempts have been made to use photo-chemical detectors other than the Schumann plate in the extreme ultra-violet. The Daguerreotype process has been tried at Harvard; the results, though interesting, are of no great practical value. It is not difficult to prepare a surface which will be very sensitive in the region about 1850 Å., and on two or three occasions records have been obtained extending to 584 Å., but in general the behaviour of the plates in the extreme ultra-violet is capricious and unsatisfactory. A really important contribution has been made by Duclaux and Jeantet.[1] They describe a way of "Schumannising" an ordinary dry plate by treating it with sulphuric acid; but the method which they prefer and which is described in their article is of a different character. Their experiments were confined to the part of the spectrum which may be investigated with a quartz spectrograph, but their results have now been extended into the region of the shortest wave-lengths.[2]

The process is extremely simple. A rather slow commercial plate, such as the Central Contrast Lantern Slide, is dipped in a solution composed of about ten drops of colourless paraffin oil dissolved in 40 c.c. of benzin petroleum (petroleum ether); it is then exposed in the usual way in a vacuum spectroscope, washed with petroleum ether, and developed. The results are nearly, though not quite, as good as those obtained with the most sensitive Schumann plates prepared according to the old method. It is easy to get a strong spectrum as far as wave-length 500 Å.

The success of the process evidently depends on fluorescent action; a number of different oils have been tried; many were found to work well, but "Nujol," a pure oil used in this country for medical purposes, may be recommended.

A fast commercial plate is not very suitable for the process because of its tendency to fog; coating a Schumann plate

[1] "Journal d. Phy.,"2, p. 156, 1921.
[2] Lyman, "Nature," 112, p. 202, 1923.

with oil does not increase its sensitivity in the extreme ultra-violet.

It is important to note that while the properties of the Schumann plate render it unfit for use in photometric work, the oil-coated plate appears to possess a satisfactory characteristic.[1] It may be possible, therefore, to carry photographic photometry into the extreme ultra-violet, thanks to the invention of Duclaux and Jeantet.

Attempts to improve the performance of Schumann plates by changes in the constitution of the emulsion or by modifications in the method of manufacture have not met with much success. After a good deal of experimenting, the writer now follows the procedure exactly as first described by its inventor. It must be noted, however, that Leifson [2] states that a reduction by one-half in the gelatine used results in an increased sensitivity.

Owing to the short focus of most vacuum spectrographs, it is difficult to bend a glass plate to the curvature necessary to bring its entire length to perfect focus at the same time without grave danger of breaking. For this reason some workers prefer to use films coated with a Schumann emulsion. Hopfield [3] has devised a method according to which such films may be prepared. They may also be purchased of Adam Hilger, of London. It should be remembered, however, that particular precautions must be taken to guard against the effects of the contraction to which these films are subject when placed in a vacuum.

[1] Harrison, " Journal Optical Soc. Am.," 11, p. 341, 1925.
[2] " Astrophysical J.," 63, p. 75, 1926.
[3] " Phy. Rev.," 20, p. 575, 1922.

CHAPTER II.

ABSORPTION AND REFLECTION IN THE EXTREME ULTRA-VIOLET.

I. ABSORPTION OF SOLIDS.

As has been already stated on page 15, quartz, rock-salt, and fluorite are the only substances which, occurring in clear masses of sufficient size, give promise of marked transparency in the ultra-violet. Of these three, fluorite is greatly the superior. Schumann investigated the behaviour of crystalline quartz early in his work,[1] and ultimately became convinced that, if very thin pieces were employed, they would be found transparent to the neighbourhood of λ 1500.[2] Subsequent observations have confirmed and extended these results, for it appears from work done with the grating spectroscope that a piece of crystalline quartz ·2 mm. thick allows a considerable amount of light to pass down to the region of λ 1450. The absorption increases rapidly with the thickness, however, a piece 2 mm. thick cutting off the spectrum near λ 1600 and greatly weakening the region between this point and λ 2000. This behaviour is clearly shown in spectra 4, 5, and 6, Plate I, "Astrophysical Journal," 25, p. 45, 1907.

These results are in agreement with some rough measurements made by Handke.[3]

Fused quartz varies greatly in transparency. The best is somewhat less transparent than the crystalline material, while some specimens measured by Pflüger are quite opaque on the more refrangible side of λ 2000.

[1] "Ber. Wien. Akad.," 102, II*a*, p. 455.
[2] "Smithsonian Contributions," 1413, p. 2.
[3] "Inaug. Dis. Berlin," 1909.

Rather rough measurements made with the prism-mirror vacuum spectroscope [1] on fourteen specimens of crystalline quartz in pieces 1 and 2 mm. thick, some selected from right-handed and some from left-handed pieces and some from specimens cut parallel and perpendicular to the optic axis, showed no difference in transparency which could be traced to the direction of rotation or to the position of the optic axis. If it were possible to apply the more refined method of Pflüger to specimens of this kind in the Schumann region, slight differences would probably be observed, corresponding to those which exist in the ultra-violet.

On examining rock-salt with the grating spectroscope, it was found that it did not fulfil its promise of transparency in the Schumann region. The spectrum does not extend beyond λ 1750. The observations have been often repeated with various samples, but always with the same result. Handke has confirmed this observation.

The factor which determined the extreme ultra-violet limit of the spectrum as obtained by Schumann was the absorption of the clear, colourless fluorite which formed the lenses and prisms of his apparatus. This fact was demonstrated with the vacuum grating spectroscope, for with this instrument it was possible to extend the spectrum considerably by removing all fluorite from the light-path. The phenomenon is illustrated in Plate II, "Astrophysical Journal," 23, p. 205. Without fluorite the limit of the spectrum in this plate lies near λ 1030; with fluorite it is cut off at λ 1230. More recently, Leifson [2] has been able to obtain the line 1215·6 through two fluorite windows.

Though clear, colourless fluorite is rare and expensive, the coloured varieties are common enough, and sometimes may be obtained in clear masses of considerable size. Stokes [3] examined one coloured specimen that showed considerable transparency in the region of λ 1850. Specimens cut from purple, green, pink, and yellow fluorite of various shades have been tested both with the grating spectroscope and with the cruder

[1] "Astrophysical J.," 25, p. 45, 1907. [2] *Ibid.*, 63, p. 76, 1926.
[3] "Collected Works," IV, p. 221.

prism-mirror apparatus. They were usually in the form of plates from 1 to 2 mm. thick. They show a considerable range of transparency. A typical spectrum taken through a purple fluorite terminates abruptly at λ 1700. Of fifty-seven specimens, forty-two were less transparent than this purple sample, ten were nearly equal to quartz 1 mm. thick, and five were almost as good as colourless fluorite from Zeiss. From this test it appeared that the depth of colour was a good indication of the absorption; the most deeply coloured were the most opaque, while the five most transparent pieces were nearly, if not quite, colourless. There was one notable exception to this rule, however; four specimens from a light green crystal from Westmoreland, New Hampshire, U.S.A., were nearly as transparent as the plates from Zeiss. This crystal was free from flaws. There is some hope, therefore, that coloured fluorite may yet be found which will serve for prisms and lenses, and which will possess the requisite transparency for use in the region between λ 2000 and λ 1250.

It is well known that the colour may be removed from fluorite by heating, and, if the process is carefully carried on, no cracks are developed. This loss of colour, however, is accompanied by only the very slightest gain in transparency, if any. In ten cases out of twelve no difference could be noted at all, either by the visual or by the photographic method.

A microscopic examination with a power of 200 diameters showed little difference in constitution between the transparent Westmoreland fluorite and the more opaque coloured varieties. In general, the specimens which showed the greater absorption seemed to contain the larger number of those fluid-filled cavities which have been so often observed. The colourless variety of fluorite from Zeiss was quite free from these microscopic enclosures.

The fluorescence excited by cathode rays was somewhat less brilliant in the colourless than in the coloured fluorite, but the differences were not of such a magnitude as to give an indication of the relative transparencies of the specimens. Recently, specimens of white fluorite from Zell in Baden have

been examined. Some of them yield plates as transparent as the material obtained from Zeiss.

Though for the construction of prisms and lenses it is necessary that the material should be obtainable in large homogeneous masses, yet for the construction of the windows for vacuum tubes, relatively small pieces are often very useful. With the hope of finding material which would serve this purpose, a variety of substances have been examined. The results may be summarized as follows :—

Topaz.[1]—Next to crystalline quartz, topaz from Ceylon shows the greatest transparency of all the substances examined. The result obtained from the photographic method shows that the spectrum is cut off near λ 1575. The specimen was 1·5 mm. thick; it is thus inferior to quartz. Topaz from Japan, Utah, and Siberia is much less transparent than this specimen from Ceylon. It is possible, however, that this difference may be considered rather as a peculiarity of the individual specimen than as a distinctive property connected with a region.

Gypsum.—This substance, when examined in bits 1 mm. thick, bounded by cleavage surfaces, shows a spectrum which extends to the region between λ 1700 and λ 1650.

Celestite.—This substance, when examined in polished pieces 1 to 2 mm. thick, shows a transparency about equal to that of gypsum.

Barite.—In polished pieces 1 to 2 mm. thick the transparency is about equal to that of rock-salt.

Alum.—Pieces cut from crystals and 1 mm. thick show a spectrum ending near λ 1750, but of rather stronger intensity than that obtained with the rock-salt.

Colemanite.—Transparent to the neighbourhood of λ 1750.

Sugar.—Plates 1 mm. thick cut from crystals of rock candy are less transparent than colemanite.

The test pieces of all the substances just mentioned were clear and free from flaws. The surfaces were carefully polished.

In addition to the above, the following substances were

[1] "Astrophysical J.," 25, p. 45, 1907

tested and found perfectly opaque to light of shorter wave-lengths than 2000: borax, adularia, calcite, chrysoberyl, sanidin, arragonite, apophyllite, silver chloride (horn silver), kunzite, and diamond. Several of these are known to be opaque to light of longer wave-lengths than 2000. The tests were made in the hope of discovering some material which showed selective absorption to a marked degree.

In the case of diamond we have an example of a crystalline substance which is transparent to the visible part of the spectrum and to X-rays, yet which is apparently opaque to light of short wave-length.

Fritsch [1] and Zschimmer [2] have both called attention to the transparency of boric anhydride for ultra-violet light. Fritsch states that, as far as he could observe in a qualitative way with a quartz spectrograph, boric oxide (B_2O_3) exerted no absorption in the region of short wave-lengths. As a result of the observations with the vacuum grating spectroscope, it appears, however, that boric anhydride in thicknesses of 1 or 2 mm. is not transparent, for practical purposes, to light of shorter wave-length than λ 1700. This substance is, therefore, of the same order of transparency as purple fluorite. It is less transparent than quartz of the same thickness.

Water.—Quantitative measurements of the absorption of pure water on the edge of the Schumann region have been made by Kreusler.[3] He gives the following results: λ 1860, absorption 68·9 per cent; λ 1930, 24·5 per cent; λ 2000, 14·2 per cent. It was found that, owing to the impurities communicated to the water by the vessel, concordant results could be obtained only when a hard glass trough was employed. The length used in the final experiments is not clearly stated; it was apparently of the order of 2 cm.; the vessel was, of course, closed with quartz windows.

Qualitative measurements have been made at Harvard [4] with layers of distilled water in vessels of glass 0·5 mm. and

[1] "Physikal Zeitsch.," 8, p. 518, 1907.
[2] *Ibid.*, 8, p. 611, 1907.
[3] "Ann. d. Phy.," 6, p. 420, 1901.
[4] Lyman, "Nature," 8 July, 1910.

1 mm. thick, closed with fluorite windows. The cells were introduced into the vacuum grating spectroscope in the same manner as when the transparency of solid substances was under investigation. Even with a prolonged exposure, the ·5 mm. water layer cut off the spectrum at λ 1729. Though the water used in these experiments was distilled, no particular precautions were taken.

Experiments in which the intensity of the Schumann light given off from a hydrogen tube was measured by the ozone which it produced, indicated that in equal layers water was much more opaque than air, but that the absorption of the water increased less rapidly than that of the air as the thickness of the layer was increased.

Data on the transparency of all other liquids on the more refrangible side of λ 1850 are lacking. Such liquids as have been examined in the region of λ 2000 show great absorption.

Celluloid.—Miss Laird has made qualitative measurements on the transparency of thin celluloid films; she employed Millikan's vacuum spectroscope with the carbon vacuum spark as source. She states that with a film 30 to 40 $m\mu$ thick it was estimated [1] that, from λ 1700 to λ 900, 50 to 20 per cent of the light was transmitted; below λ 900, not much over 5 per cent. The transmission was followed to λ 450, and was thought to extend lower. Miss Laird has also made the extremely interesting observation that *silver foil* ·00002 cm. thick transmitted the strong lines to λ 900; two layers did the same, but the lines below λ 1140 were very faint.

Further investigations on this subject are much to be desired.

Dispersion of Fluorite.

The dispersion of fluorite has been calculated by a number of physicists.[2] Of the earlier of these results in the extreme ultra-violet, those of Martens [3] have proved to be, perhaps,

[1] "Physical Rev.," 29, p. 41, 1927.
[2] Kayser, "Handbuch," IV, p. 477.
[3] "Ann. d. Phy.," 6, p. 619, 1901.

most nearly in agreement with the facts. The data were obtained from a formula of the Kettler-Helmholtz type involving two absorption bands, the one in the red, the other at λ 951·9. From a knowledge of the dimensions of Schumann's apparatus, and by the use of these calculated indices, Martens estimated that the extreme point reached by Schumann had a wave-length of λ 1250; a result which subsequent measurements have shown to be very near the truth.

Handke,[1] using a prism spectroscope of the Schumann type and employing the values of the wave-lengths of the hydrogen spectrum determined at Harvard University, measured the index of refraction for fluorite to wave-length λ 1311. In order to make the results of experiment agree with calculation, he found it necessary to introduce two absorption bands in the extreme ultra-violet in the dispersion formula, one at λ 1056, the other near λ 610. Handke's values may be found in the fifth edition of the Landold-Börnstein Tables (p. 911). The refractive indices of quartz [2] and rock-salt have been determined only to λ 1854.

II. THE ABSORPTION OF GASES.

The air was the first gas whose absorption was investigated by Schumann. It will be well, therefore, to begin with a general account of its behaviour in the region of extremely short wave-lengths before turning to the absorption of other gases.

Kreusler [3] found that a column of dry air 20·45 cm. long, free from carbon dioxide, absorbed 8·8 per cent of the light at wave-length λ 1860. At wave-length λ 1930 the absorption was so small that it could not be measured.

Schumann [4] examined the effect of change of thickness of the absorbing column; he employed the device which has already been described, whereby the length of the absorption layer could be varied continuously. He used as source a

[1] "Inaug. Dis.," Berlin, 1909.
[2] Kayser, "Handbuch," IV, p. 484.
[3] "Ann. d. Phy.," 6, p. 418, 1901.
[4] "Smithsonian Contributions," 1413, p. 29.

discharge tube giving the spectrum of carbon dioxide. He found that the limit of the spectrum remained in the neighbourhood of wave-length 1780, while the path was reduced from 15 mm. to 8 mm. It was only when a length of 4 mm. was reached that the spectrum began to extend. From this point onwards the extension was much more rapid; with an air thickness of ·5 mm. the last visible wave-length was in the neighbourhood of λ 1630. He carried his observations to air strata as thin as ·05 mm. and showed that under these circumstances the spectrum stretched considerably beyond λ 1600. As the dispersion of fluorite had not been experimentally determined at this time, Schumann's wave-lengths were obtained by a process of extrapolation, a method which yielded only approximate results to the neighbourhood of λ 1600, and which completely broke down on the more refrangible side of this region. However, measurements on the absorption of air, carried on at Harvard University [1] by a method in which the limiting wave-lengths could be accurately determined, have served to confirm Schumann's observations to a marked degree.

It is important to note in this connexion how short must be the stratum of air in order that the region in the neighbourhood of λ 1600 may be transmitted. Before considering the behaviour of the air at the more refrangible limit of the Schumann region, it will be most convenient to take up the absorption of some of its constituents.

Nitrogen.—Kreusler [2] found that nitrogen absorbed 2·2 per cent at wave-length 1860; the presence of small quantities of nitrous oxide (NO) increased the value very considerably. Schumann [3] states that "nitrogen proved itself very transparent, even beyond λ 1620, yet it absorbed particular wave-lengths very energetically." Experiments with the grating vacuum spectroscope [4] and a vessel 9·14 mm. long showed that at atmospheric pressure nitrogen produces a very slight absorption, extending continuously from λ 1800 or

[1] Lyman, "Astrophysical J.," 27, p. 89, 1908.
[2] "Ann. d. Phy.," 6, p. 418, 1901. [3] Loc. cit.
[4] "Astrophysical J.," 27, p. 93, 1908.

thereabouts to λ 1250. The strength of this absorption increases regularly with decrease in wave-length, but even at the most refrangible end of the spectrum it is very small indeed. The energetic, selective action mentioned by Schumann was not observed.

Leifson [1] has employed a cell with fluorite windows, a hydrogen tube as source, and a vacuum grating spectroscope. He finds that the absorption of nitrogen is in the form of a band, with a maximum at λ 1440. With a layer of the gas 5 mm. thick at atmospheric pressure, this band extends from λ 1520 to λ 1370. When the pressure in the absorption cell is reduced to one-fifth of an atmosphere, the absorption is no longer noticeable. Leifson attributes the selective absorption observed by Schumann to the presence of nitric oxide. He himself used commercial nitrogen, purified by hot copper dust and dried over phosphorous pentoxide.

Hopfield [2] studied the absorption of nitrogen by introducing the gas directly into the body of his vacuum grating spectroscope. He says that from considerations of the dimensions of the spectrograph and the pressure of the gas, it is evident that a layer of nitrogen 4·5 cm. thick at atmospheric pressure is easily transparent to λ 1070. Strong continuous absorption begins at λ 990.[3] In all probability it was the nature of the source which he used which prevented him from observing the band discovered by Leifson. Sponer,[4] using Hopfield's method, recently discovered nine bands, the first member of the group at λ 1449·9, the last at λ 1226·6. The first three members lie within the region occupied by the great band, as given by Leifson.

Oxygen.—This gas is the dominating factor in determining the transparency of the air. Kreusler [5] ascribes an absorption of 32·5 per cent at λ 1860, 6·2 per cent at λ 1930, and a negligible absorption at λ 2000; the column was as usual 20·45 cm. long. Schumann makes the following statement:

[1] "Astrophysical J.," 63, p. 73, 1926.
[2] "Phy. Rev.," 20, p. 582, 1922. [3] *Ibid.*, 29, p. 356, 1927.
[4] "Proc. Nat. Acad.," 13, p. 100, 1927.
[5] "Ann. d. Phy.," 6, p. 418. 1901.

" Oxygen absorbs the rays in the neighbourhood of λ 1850 in a series of clearly resolved groups of lines, fourteen in number. These groups, which are of band-like form, constantly approach nearer one another with the deviation, and are shaded off toward the red. Complete absorption is found with the most refrangible of them. It is this which makes the air opaque for all rays beyond λ 1850."

The earlier work which was done with the grating in vacuum has thrown much valuable light on the absorption of oxygen, but failed to prove conclusively the existence of these groups of lines near λ 1850. This failure was probably due to the difficulty which was experienced in obtaining a continuous spectrum from a discharge tube in the neighbourhood of λ 1850, and to the fact that, though the slit employed was a good one, yet it fell far short of the perfection of the slit employed by Schumann.

These absorption lines are of particular interest in connexion with the lines or bands observed by Steubing.[1] This investigator, using a mercury arc in quartz as a source and a quartz prism spectroscope in air, designed to give a great deal of light in the ultra-violet, obtained three groups of bands extending from λ 1919 to λ 1831. He attributes the phenomenon to the fluorescence of the layer of oxygen between the source and the slit of the spectroscope. These same bands have been observed with the vacuum grating spectroscope at Harvard when a mercury arc was employed as source.[2] Unfortunately, the construction of the grating apparatus did not permit the observer to decide definitely whether these bands were really due to the fluorescence of oxygen in front of the slit or to the absorption of the oxygen within the apparatus. More recently, Messrs. L. & E. Bloch[3] have studied the phenomenon. They conclude that the bands are due to the absorption of oxygen, not to its fluorescence.

The work of Leifson[4] has put our knowledge of the subject

[1] " Ann. d. Phy.," 33, p. 572, 1910.
[2] Lyman, " Astrophysical J.," 38, p. 284, 1913.
[3] " Comptes Rendus," 158, p. 1161, 1914.
[4] " Astrophysical J.," 63, p. 73, 1926.

on a definite basis. With an absorption chamber 25 mm. thick, and with dry commercial oxygen at 740 mm. pressure, he obtained fourteen bands. The position of the heads is expressed fairly accurately by the relation

$$v = 56931 - 76{\cdot}63\ m - 20{\cdot}05\ m^2.$$

They extend from λ 1756·7 to λ 1924·8.

The five heads at λ 1846·9, 1864·2, 1883·0, 1903·1, and 1924·8 undoubtedly are those observed by Steubing.

Leifson has investigated the fine structure of four of these bands.

Duclaux and Jeantet[1] used an absorption cell 50 cm. thick with oxygen at atmospheric pressure. They found four bands between λ 2000 and λ 1900. They designate them as belonging to Group II, and show that they are similar in nature to the Schumann bands which they call Group I. They found that there was a constant frequency difference between the corresponding bands of the two groups.

It appears, therefore, that the absorption of oxygen in the extreme ultra-violet is characterised by two groups of narrow bands extending from the neighbourhood of λ 2000 to λ 1756, followed by a wide region of continuous absorption.

All the measurements on the great oxygen band carried out at Harvard were made with an absorption chamber of constant thickness (·9 cm.), the amount of absorption being varied by changing the pressure within this chamber. The discovery of the extreme ultra-violet limit of the band was the most striking product of these experiments.[2] A discharge tube filled with a mixture of carbon dioxide and hydrogen served as source. A series of exposures was then made on the same plate, with different pressures in the absorption chambers. Thus the uppermost spectrum was secured when the pressure in the chamber was a few hundredths of a millimetre, the succeeding spectra with pressures of ·02, ·05, ·07, ·1, ·25, 0·5, and one atmosphere respectively. The lowest spectrum was taken under the same conditions as the upper-

[1] "Comptes Rendus," 173, p. 581, 1921.

[2] Compare Plate VII, Lyman, "Astrophysical J.," 27, p. 87, 1908.

most. The character of the band is unmistakable. With a pressure of ·1 atmosphere, the more refrangible limit is not visible in the reproduction, though it can be just made out in the plate itself; but as the pressure in the absorption chamber is decreased, this limit comes into view. Most unfortunately, a more careful study of the more refrangible region is much interfered with by the absorption of the fluorite windows, which first begins to be noticeable near λ 1300. There was, however, some indication that another absorption band existed, lying in the region shut out by the opacity of the fluorite.

These conclusions have been confirmed, and our knowledge of the subject has been much extended by the work of Hopfield.[1] He introduced oxygen into the whole of his apparatus; thus, while the spectrum was being photographed, a steady stream of gas was kept flowing through the body of the spectroscope and into the discharge tube. In this way the gas under examination served both as the source of light and as the absorbing substance.

The remarkable fact appears that beyond the great absorption band a short region of considerable transparency exists in oxygen. Hopfield states that the gas in a column 3·3 cm. thick and at atmospheric pressure transmits a group of lines which includes the wave-lengths λ 1100 and λ 1217·7.

Beyond this window in the spectrum there is a second absorption band whose extreme ultra-violet limit has not been exactly determined. Hopfield has been able to photograph an emission line at λ 507·2 by reducing the pressure in his whole apparatus to ·04 mm., which shows that this second band slowly fades away with reduced pressure.

The unsymmetrical character of the first broad band is very striking, for, with increase in pressure, the absorption spreads much more rapidly toward the less refrangible side than in the other direction. Unsymmetrical effects of this kind are not uncommon. Such a band exists in chlorine, as was shown by Miss Laird,[2] and more recently Wood[3] has

[1] "Phy. Rev.," 20, p. 573, 1922.

[2] "Astrophysical J.," 14, p. 114, 1901. [3] *Ibid.*, 26, p. 41, 1907.

called attention to the same phenomenon in an absorption band in mercury.

The transparency of oxygen in the neighbourhood of λ 1200 has an important bearing on the optical behaviour of air in the extreme ultra-violet. Hopfield says: "It has already been shown that nitrogen is equally transparent in this region in layers 4·5 cm. thick. Hence air has a remarkable transparency in this region of short wave-lengths, for if one uses as the basis of reckoning the proportion of oxygen and nitrogen in the air, it is seen that the absorption equivalent of the above-mentioned thicknesses of oxygen and nitrogen when mixed in air is a layer 4·2 cm. thick. This fact recalls an observation of Lenard,[1] who detected a fluorescence about an aluminium spark in air that extended to a distance of 4 or 5 cm. from the source. The above-mentioned facts of the short waves of lengths 1100 to 1218 Å. being able to penetrate that thickness of air, would explain the fluorescence. They are probably not the same rays that penetrated both quartz and fluorite as stated by him."

Ozone.—The formation of ozone has been studied by a number of observers in the ultra-violet, but as observations on the action of Schumann light are not common, a description of some experiments on the subject may be of interest here.[2]

A discharge tube of the internal capillary type, Fig. 6, was filled with hydrogen to about 1 mm. pressure, and closed by a fluorite window. The tube was excited by a transformer; the current in the secondary was of the order of 10 milliamperes. Under these conditions the gas showed the many-line spectrum of hydrogen. The following experiments were then tried:—

1. Half of the fluorite window was protected by a piece of microscope cover glass, and over it was laid a bit of paper moistened with starch paste containing potassium iodide; in fifteen seconds the paper turned strongly blue where it was

[1] "Sitz. Heidelburg Akad. d. Wiss. Abhand.," p. 31, 1910.
[2] Lyman, "Astrophysical J.," 27, p. 87, 1908.

not protected by the glass, the protected portion remaining perfectly unaltered.

2. A piece of quartz 2 mm. thick was next placed on the fluorite window so as completely to cover it; the test paper was placed on the quartz. In fifteen seconds there was a noticeable discoloration of the paper, but the effect was not nearly so well marked as in case 1.

3. A shallow vessel, B, with a fluorite bottom was next placed directly upon the discharge tube so that the two fluorite

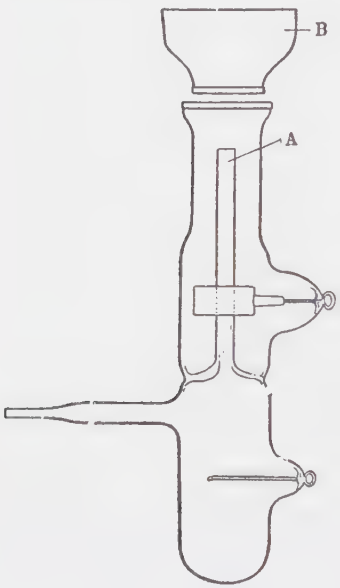

FIG. 6.

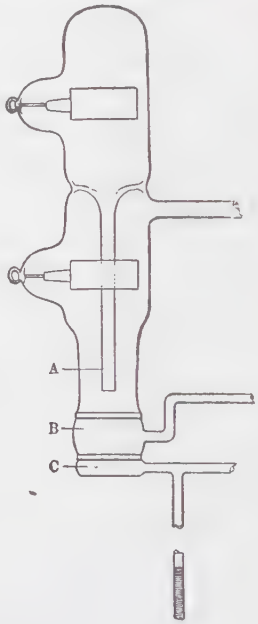

FIG. 7.

plates were in contact. The test papers placed within this vessel upon the fluorite bottom showed in fifteen seconds a discoloration only slightly less than that observed in case 1.

4. The vessel, B, was now raised $\frac{1}{2}$ mm. above the window of the tube; thus the light was forced to penetrate a column of air $\frac{1}{2}$ mm. thick in addition to the fluorite plates; the discoloration of the paper in fifteen seconds was now very slight.

5. If the vessel was removed to a distance of 1 mm., no discoloration could be observed. It is evident that the agency

which produced the discoloration is weakened by quartz and is, so far as these experiments show, entirely cut off by 1 mm. of air. There can be but little doubt that the agency is light of a shorter wave-length than λ 1850.

A more elaborate experiment was next undertaken. A discharge tube had, cemented upon its fluorite window, a chamber, B, Fig. 7, 0·7 cm. thick; this chamber in turn was closed by a fluorite window which carried a second shallow vessel, C, 0·1 cm. thick. This last vessel was connected to a manometer column which dipped in strong sulphuric acid. The function of the chamber, B, was to serve as a screen of variable transparency, and to this end it was connected to a mercury pump and McLeod gauge. The discharge tube was filled with hydrogen at about 1 mm. pressure. The vessel, C, was filled with oxygen at atmospheric pressure. No change in the manometer column was observed when the discharge tube was excited. It was only when the pressure in B had been reduced to about 1 cm. that the acid in the manometer column began to rise; but this rise continued to increase as the pressure in B was reduced step by step. Care was taken to correct as far as possible for heat effects.

The results with this more complex apparatus serve to corroborate the results of the simpler experiment. There seems to be no doubt that light of wave-lengths shorter than λ 1850 acts to produce chemical action energetically, and that this action increases considerably in strength with decrease in wave-length in the region more refrangible than λ 1850. It must be remarked, however, that the starch-paper test cannot distinguish, any more than the manometer, between the production of ozone and hydrogen peroxide. The gas formed may be either the one or the other.

As to the absorption of ozone in the extreme ultra-violet, Schumann remarks,[1] speaking of oxygen: "The pressure of a moderate amount of ozone did not alter the absorption at all." Experiments with the grating spectroscope confirm this statement.[2]

[1] "Smithsonian Contributions," 1413, p. 16.

[2] Lyman, loc. cit.

Carbon Dioxide.—Kreusler [1] attributes 13·6 per cent absorption to this gas at λ 1860. Schumann [2] states that the absorption spectrum is similar to that of oxygen, with an indication of a "rhythmical series in the shape of inverted groups of lines, but the end of this series is considerably more refrangible than that of oxygen. Accordingly, total absorption begins at a shorter wave-length." The first observations made with the vacuum grating spectroscope were in very fair agreement with the statement made by Schumann, except that the rhythmical series was not observed near λ 1850. There were also some indications that maxima and minima of absorption do occur considerably on the more refrangible side of this position.

Leifson [3] states that with a cell 15 mm. thick and carbon dioxide at atmospheric pressure there was no noticeable absorption above λ 1712. At this point absorption was found to begin in the form of bands shaded off toward the red; they are presumably the bands already mentioned. There is considerable general absorption which makes these bands indistinct. Total absorption begins at λ 1610. When the pressure in the cell was reduced to one-fifth of an atmosphere, the selective absorption appears to extend from λ 1600 to the limit of transparency of fluorite. The gas was prepared from calcium carbonate and hydrochloric acid, washed with sodium bicarbonate, and dried over phosphorous pentoxide.

Carbon Monoxide.—According to Schumann,[4] this gas absorbs the most refrangible rays somewhat less than carbon dioxide, and gives, like oxygen, a series of rhythmical, inverted groups of lines. The clearness and sharpness of these lines are less than with oxygen, but far more perfect than with carbon dioxide.

On the other hand, results obtained with a grating showed that the absorption is very characteristic and quite unlike that of oxygen, at least in the more refrangible part of the Schumann region.[5] There seems to be very little action from

[1] "Ann. d. Phy.," 6, p. 418, 1901.
[2] Loc. cit.
[3] "Astrophysical J.," 63, p. 84, 1926.
[4] Loc. cit.
[5] Compare Plate VII, Lyman, "Astrophysical J." 27, p. 87, 1908.

λ 1850 to λ 1600, but from λ 1650 to λ 1250 eight separate bands exist. The maxima occur near λ 1548, 1512, 1482, 1450, 1423, 1395, 1370, 1345. For any given pressure the bands decrease in width with decrease in wave-length. As the pressure is reduced, each band contracts, but even at a value of 0·1 of an atmosphere, all the bands are still distinguishable. They do not correspond to any lines or groups of lines in the emission spectrum of the gas. At least two of the bands seem to coincide with those observed in carbon dioxide. The limit of the spectrum, as shown in the illustration, is not due to absorption but to the character of the source of light.

As in the case of oxygen, the lack of a continuous spectrum in the source near λ 1850 probably accounts for the failure to detect the rhythmical groups of lines with the grating. Schumann confined his attention in almost all his absorption work to the region on the less refrangible side of λ 1600; this may explain the fact that he did not observe the characteristic bands just mentioned.

All the early experiments with the grating were made with a single gas thickness of ·91 cm.

Leifson,[1] using an absorption cell of 15 mm., has extended these results, adding four bands to the eight mentioned above. The wave-numbers of this group of twelve members are given by

$$v = 64678 + 1487{\cdot}5\ m - 15{\cdot}92\ m.^2$$

He calls attention to the existence of a faint band of uncertain character between λ 1820 and λ 1760. His gas was prepared from oxalic and sulphuric acid, passed through a strong solution of potassium hydroxide, and dried.

Hopfield [2] introduced carbon monoxide into the receiver of his spectroscope; by gradually varying the pressure from ·05 to 850 mm. he obtained nine absorption systems between λ 920 and λ 2064.

The Inert Gases: Helium.—This substance has been investigated with the vacuum grating spectroscope.[3] In thickness

[1] "Astrophysical J.," 63, p. 73, 1926.
[2] "Phy. Rev.," 29, p. 922, 1927.
[3] Lyman, loc. cit.

of ·91 cm. at atmospheric pressure, the gas shows no observable absorption in any part of the spectrum between λ 1900 and λ 1250. Experiments with a gas path of 6·5 cm. at ¾ of an atmosphere show that helium is quite as transparent as hydrogen under the same conditions.

More recent investigations [1] show that helium probably possesses a continuous spectrum in emission beyond the limit of the principal series; this indicates that continuous absorption exists below λ 504; the lack of a suitable light source prevents the experimental investigation of this point.

Cuthbertson [2] has computed the position of the absorption bands in the inert gases from refraction and dispersion data in the visible. He makes use of Drude's dispersion equation, and assumes that there is only one free frequency in the molecule. In this way he finds the following values: helium, λ 507; neon, λ 481; argon, λ 726; krypton, λ 840; xenon, λ 1001.

His attempts to confirm these results by experiment cannot be regarded as very satisfactory; as he himself is at pains to point out, his method is beset by several serious difficulties. A grating of about 48 cm. was employed, the source was a carbon arc, the gas to be studied was introduced directly into the body of the spectroscope, and came in contact with the source; attempts to use a window of celluloid failed. The value of the results is greatly impaired by the possibility of impurities in the gas, either originally present, or derived from the arc or from the walls of the spectroscope. Cuthbertson states that the broad result of the work is to confirm, though somewhat roughly, the predictions of the simplest form of the theory of dispersion.

Neon was the most transparent of all the inert gases examined: with a pressure of half a millimetre in the apparatus lines were visible at λ 595.

Spectroscopic investigations [3] lead to the conclusion that

[1] Lyman, "Astrophysical J.," 60, p. 1, 1924.

[2] "Proc. Roy. Soc. Lond.," 114, p. 650.

[3] Dorgelo and Abbink, "Zeits. f. Phy.," 41, p. 764, 1927, and 47, p. 221, 1928.

strong absorption in the inert gases should begin at the following points in the spectrum: Neon, λ 575; argon, λ 786; krypton, λ 888; xenon, λ 1029. The presence of absorption beyond these wave-lengths has been found by direct observation for argon,[1] krypton, and xenon. With the exception of neon, the figures are in fair agreement with the values calculated from dispersion data by Cuthbertson.

In a test made at Harvard some time ago argon showed no observable absorption between λ 1900 and λ 1250 in a column ·91 cm. long at atmospheric pressure.

Hydrogen.—Schumann [2] recognized that the transparency of hydrogen was uncommonly great in the region bounded by the transparency of fluorite. Upon this observation he based the procedure of washing vacuum spectroscopic apparatus with this gas. He calls attention to the fact, however, that it is extremely difficult to obtain information on the behaviour of thick strata of the gas because of the impurities communicated to it by the walls of the containing vessel employed. "These impurities affect the transparency of the hydrogen more, proportionally, than they would that of other gases, precisely because its transparency is so extraordinarily great." [3]

The results early obtained with the vacuum grating spectroscope were in good agreement with these facts. When the gas was used in the ·91 cm. absorption chamber at atmospheric pressure, it exercised no observable absorption.

The longest gas path which was examined under conditions that reduced the chances of contamination to a minimum was 6·5 cm. Here [4] the light from a spark contained in a glass vessel passed through hydrogen at atmospheric pressure. A number of spark spectra, extending nearly to the limit set by the transparency of fluorite, were obtained in this way.

The work of Dieke and Hopfield [5] has extended and corrected our knowledge of the subject. They introduced

[1] Dorgelo and Abbink, loc. cit.
[2] "Ann. d. Phy.," 4, p. 642, 1901.
[3] "Smithsonian Contributions," 1413.
[4] Lyman, "Astrophysical J.," 35, p. 344, 1912.
[5] "Phy. Rev.," 30, p. 400, 1927.

hydrogen into the body of their spectroscope; a source producing a continuous spectrum was employed; discharge tube and spectroscope were exhausted by two separate pumping systems; by this arrangement a considerable difference of pressure could be maintained between the source and the vessel in which the absorption took place.

They find that the absorption spectrum of the hydrogen molecule consists of a series of bands arranged in a regular manner, beginning near λ 1115, and extending toward the region of shorter wave-lengths; these bands are of the same type as those of the emission spectrum. Strong continuous absorption sets in near λ 850.

Water Vapour.—Data on this substance in the extreme ultra-violet are lacking. Schumann did not succeed in obtaining any information. Experiments with the grating apparatus indicated a maximum of absorption between λ 1700 and λ 1600, with some promise of transparency on both sides of this region, but the results are rather doubtful. The formation of opaque films of water on the windows of the absorption cell is the factor which causes the uncertainty.

Leifson [1] states that the strong band extends from λ 1780 to λ 1610, with a maximum at λ 1700. At λ 1392 a second band begins; its limit on the side of shorter wave-lengths lies beyond the range of observation as set by the transparency of fluorite.

The results which follow for nitrous and nitric oxide, for nitrogen peroxide, hydrogen chloride, ammonia, methane, carbon tetrachloride, and ethyl alcohol vapour are taken directly from Leifson; [2] the extent of the region examined was limited by the transparency of fluorite.

Nitrous Oxide.—This gas was prepared by heating ammonium nitrate and dried with phosphorous pentoxide. The absorption cell had a thickness of 15 mm.

Nitrous oxide shows no selective absorption in the Schumann region. With this gas in the cell at atmospheric pressure, the absorption is in the form of two continuous bands,

[1] "Astrophysical J.," 63, p. 73, 1926. [2] Loc. cit.

the first extending from λ 2000 to λ 1680, and the second from λ 1550 beyond the range of observation.

Nitric Oxide.—This gas was prepared by dropping concentrated nitric acid into a boiling solution of ferrous sulphate and dilute sulphuric acid. It was dried with phosphorous pentoxide. The absorption cell had a thickness of 15 mm.

Exposures were made with nitric oxide in the absorption cell at pressures of 0·01, 0·1, and 1 atmosphere. The spectra obtained show a large number of narrow bands. Those on the less refrangible side of λ 1800 are double. There was no observable continuous absorption. The bands seem to form no regular series; a number of similar groups, however, were noted.

Nitric oxide is of particular interest as it is likely to occur as an impurity in nitrogen; some of the bands just mentioned have been attributed to the latter gas.

Kreusler [1] has shown that both nitric and nitrous oxides possess strong absorption in the ultra-violet. His measurements on the former substance give 88·4 per cent at λ 2000.

Nitrogen Peroxide.—This gas was prepared with copper and concentrated nitric acid and dried with phosphorous pentoxide. The absorption cell had a thickness of 15 mm.

Of all the gases examined in this investigation, nitrogen peroxide was found to be the most opaque. No evidence of selective absorption in the Schumann region was obtained. With this gas in the cell at atmospheric pressure all light below λ 4000 was absorbed. As the pressure in the cell was reduced to 150 and 30 mm., total absorption occurred at λ 2400 and λ 2100 respectively. When the pressure was reduced to 6 mm., two broad absorption bands appeared with maxima at λ 1700 and at λ 1400, and also a third band, extending from λ 1325 beyond the range of observation.

Hydrogen Chloride.—This gas was obtained by heating concentrated hydrochloric acid. It was dried with phosphorous pentoxide. The cell had a thickness of 15 mm.

With hydrogen chloride in the cell at atmospheric pressure,

[1] Loc. cit.

all light below λ 2350 was absorbed. When the pressure was reduced to one-fifth of an atmosphere, total absorption occurred at λ 2250; and at one-fiftieth of an atmosphere, four broad, continuous absorption bands appeared. The approximate limits of these bands are λ 2150 to λ 1850, λ 1750 to λ 1650, λ 1580 to λ 1290, and from λ 1270 beyond the range of observation. A very intense, narrow band appeared at λ 1289, when the pressure was reduced to 10 mm. At 1 mm. pressure this band was reduced to a narrow line. The change in width was symmetrical.

Ammonia.—This gas was obtained by heating concentrated ammonium hydroxide, and it was dried with calcium oxide. The absorption cell had a thickness of 15 mm.

With ammonia in the absorption cell at atmospheric pressure, there appeared three absorption bands at λ 2260, λ 2210, and λ 2166. Beyond the last band the absorption was complete. These are probably the same as those observed by Ferrières.[1] The bands increase rapidly in width with decreasing wave-length. It was therefore inferred that the apparent general absorption was really due to a long series of bands, and this inference was subsequently verified by means of an exposure with the ammonia in the absorption cell at a pressure of about 3 mm. The spectrum thus obtained shows a group of regularly spaced bands. These bands number eighteen, they extend from λ 2260 to λ 1515; a table of their wave-lengths is given in the original article. They reach across the gap, λ 1813·7 to λ 1614, but here they are too faint to be measured. No attempt was made to obtain an equation for the wave-numbers of these bands because of the irregularities in the successive differences. It seems probable, however, that the correct wave-numbers could be expressed by a polynomial of the second degree, the bands appear to decrease uniformly in intensity from the middle of the group toward both sides.

Methane.—The gas was prepared by distillation of a dry mixture of sodium acetate and soda lime. It was dried with phosphorous pentoxide; the cell had a thickness of 15 mm.

[1] "Comptes Rendus," 178, p. 202, 1924.

With this gas under a pressure of one atmosphere, all light beyond λ 1800 was absorbed. As the pressure in the cell was reduced, this limit receded toward the violet. At the lowest pressure used, 6 mm., there appeared a number of bands, with centres at λ 1558, 1528, 1501, 1474, 1448, and 1420 approximately. No attempt was made to calculate a formula for this group of bands because of uncertainty in the measurements of the wave-length.

Carbon Tetrachloride Vapour.—Pure carbon tetrachloride was used. The cell had a thickness of 25 mm.

Carbon tetrachloride vapour shows no selective absorption. With a vapour pressure of 90 mm. in the absorption cell, total absorption begins at λ 2100. As the pressure is reduced, the limit of transparency moves slowly toward the ultra-violet. With a vapour pressure of 10 mm., the absorption is in the form of two bands. The first extends from λ 1840 to λ 1670; the second begins at λ 1530, and extends beyond the range of observation.

Ethyl Alcohol Vapour.—Pure ethyl alcohol was used. The absorption cell had a thickness of 25 mm.

With this vapour at a pressure of 6 mm. in the cell, total absorption occurs at λ 1570. On the side of this limit toward longer wave-lengths there appear a number of equally spaced, narrow bands whose wave-numbers are given by the relation

$$v = 49{,}044 + 875\,m.$$

A list of the bands is given in the original paper; those at λ 1969 and λ 1936 are most intense, the intensity decreases rapidly toward both sides of the group. It is therefore probable that under more favourable conditions additional bands might be obtained with wave-lengths longer than λ 2039, and others shorter than λ 1872.

In conclusion, it is of interest to return to the behaviour of the air. It appears that the absorption of carefully dried air is almost entirely due to the oxygen and nitrogen which it contains. It is the less refrangible edge of the oxygen band which forms the barrier separating the Schumann region from the ordinary ultra-violet. However, as might be expected,

air is more transparent than oxygen, for while with oxygen at atmospheric pressure and a path of 0·91 cm. the last visible wave-length is near λ 1760, for air under similar circumstances it is near λ 1710. As one progresses toward the region of shorter wave-lengths, it becomes evident that air partly recovers its transparency, or, in other words, that the absorption is in the form of a band; but there is at least one difference to be observed between the action of the gas mixture and that of the element, for with air the more refrangible limit of the band is rather indistinct, while with oxygen at a corresponding pressure it is sharp; this effect is probably due to the presence of nitrogen. All this was known from the early work with a grating spectroscope at Harvard. More recently, Hopfield has shown that both oxygen and nitrogen are quite transparent in the region between λ 1100 and λ 1218. As has been already mentioned, he deduces from these data that a column of air 4·2 cm. thick at atmospheric pressure should have a remarkable transparency.

Continuing toward shorter wave-lengths, air becomes again opaque, as might be expected from the fact that strong continuous absorption sets in with nitrogen below λ 990. From this point onward, experimental investigation becomes increasingly difficult, largely because of the lack of a suitable source of light. That air possesses considerable opacity in the neighbourhood of λ 3, is known from experiments on soft X-rays [1]; but on the progress of its absorption curve from λ 900 toward shorter wave-lengths there is no exact information.

It seems improbable that such traces of ozone, carbon monoxide, and carbon dioxide as are ordinarily to be found in the atmosphere can have any marked effect upon its absorption for the part of the spectrum under consideration. Experience indicates, however, that the presence of water vapour tends to limit the extent of the spectrum in the extreme ultra-violet.

Before leaving this subject it is well to remind the reader

[1] Siegbahn, "The Spectroscopy of X-rays," Oxford Press, 1925, p. 61.

that data on the dispersion of gases lead theoretically to a knowledge of the position of their absorption bands. In the case of the inert gases the agreement between theory and experiment is fair (see p. 81); but Cuthbertson's[1] calculations for oxygen do not agree with the facts.[2]

REFLECTING POWER OF METALS.

Data on the reflecting power of metals on the short wave-length side of λ 1800 are very meagre.

Gardner[3] has compared the reflecting power of nine substances with that of speculum in the region between λ 1640 and λ 1030. One half of the slit of a vacuum grating spectroscope received light reflected from the substance under examination at 45°, while the other half was illuminated by rays from the same source reflected from a standard mirror of speculum; the resulting spectra were received side by side on a Schumann photographic plate.

Silicon proved much the best reflector of all the substances examined. Throughout the entire range (λ 1640 to λ 1030), it is superior to speculum; the superiority is most marked, however, between λ 1600 and λ 1300, that is to say on the side of longer wave-length.

Platinum shows no superiority over speculum between λ 1600 and λ 1300, but below λ 1300 the spectrum reflected from platinum is distinctly the stronger. Thus, the reflecting power of this substance seems to be increasing with decrease in wave-length. Stellite, copper, nickel, gold, and steel show only minor variations of reflection when compared with speculum.

Silver and aluminium are very inferior, with silver ranking above aluminium.

Pfund[4] has made some semi-quantitative measurements of reflecting power in the extreme ultra-violet. He employed a hydrogen tube so excited as to produce the atomic spectrum

[1] "Proc. Roy. Soc.," 83, p. 151, 1910.
[2] Dember, "Verh. Deutsch. Phy. Gesell.," 15, p. 564, 1913.
[3] "Astrophysical J.," 45, p. 30, 1917.
[4] "Journal Optical Soc. of Am.," 12, p. 467, 1926.

very strongly. The total radiation received from this source was first reflected from a concave glass mirror, then from the substance under examination, and was finally received on a thermopile. Since the galvanometer deflections were decreased by exactly the same amount by the introduction of glass as by the use of fluorite as a screen, Pfund concludes that no energy was present in his source in the region between the point set by the opacity of glass and λ 1300, where fluorite becomes opaque. By the use of a glass screen, therefore, he was able to correct for the effect of the visible, the violet, and the extreme ultra-violet to λ 1300. The following data are supposed to refer to the reflecting power of the various substances for a band in the spectrum between λ 1216 and λ 912 :—

Speculum, 5·2 per cent ; silver, 5·1 ; gold, 6·3 ; platinum, 8·0 ; quartz, 13·5 ; glass, 8·5.

For practical tests of reflecting power carried on directly upon gratings, the reader is referred to p. 51. It there appears that glass is distinctly superior to speculum on the short wavelength side of λ 500, but that quartz shows little superiority to glass in the same region. The importance of the effect of surface layers of grease, oxide, or even of gas is emphasised.

The rapid weakening of all spectra on the short wavelength side of λ 200 points to a correspondingly rapid decrease in the reflecting power at normal incidence of speculum, glass, and quartz.

Before leaving the subject, it is interesting to note that Pfund [1] announces selective reflection from rock-salt at λ 1547.

[1] " Phy. Rev.," 32, p. 39, 1928.

CHAPTER III.

EMISSION SPECTRA.

Fourteen years ago little had been done toward the study and classification of radiations from gases and solids in the extreme ultra-violet; in fact, the very existence of such radiations was a kind of scientific curiosity. It was natural, therefore, that in the first edition of this book the spectra of comparatively few substances were treated, and that a good deal of space was devoted to the technique of their production. Now all this has changed; a very considerable amount of data on the spectra of many elements have been accumulated, and the region of the extreme ultra-violet has come to form a continuous part of the realm to which spectroscopic measurement and speculation are applied. In order to compress the information available into the compass of so small a volume as this one, it has seemed best to confine attention to a brief description of the various spectra and to omit as far as possible details of technique. The same limitation of space precludes a detailed account of series relations. However, as hydrogen was the first substance to be studied in the extreme ultra-violet, an exception will be made in its favour, for the early investigations of its spectra possess both historic and practical interest.

Hydrogen surpasses all other gases in the wealth and strength of lines in the Schumann region; these lines extend from λ 1675 to the neighbourhood of λ 850. The general appearance of the spectrum was first investigated by Schumann to the point where fluorite absorbs strongly. Later, the spectrum was extended to nearly its present limit with the vacuum grating spectroscope at Harvard, and the wavelength of a great number of the lines was determined for the

first time. These wave-length measurements formed the earliest standards available in the extreme ultra-violet. They are given in Table I of the Appendix.

A comparison of the original prism spectrograms with the normal spectrum from the grating was made; it not only proved the identity of the two spectra but has served to supply the beautiful plates of Schumann with a scale of wave-lengths.[1] This comparison was carried out in the following manner: the twelve plates of Schumann reproduced in the "Smithsonian Memoirs" were cut out and put together. The resulting spectrum, some 127 cm. long, was placed on a movable stand and the grating spectrum was projected upon it by means of a lens. By changing the magnification so as to keep step with the dispersion, the strong lines on the one spectrum were identified with those in the other from λ 1674 to λ 1269 without the least difficulty. From the values thus obtained interpolation curves were drawn for each of Schumann's twelve plates separately, and by means of these curves a scale of Ångström units was attached to each of the twelve illustrations. Except for a short range of some fifty or sixty Ångströms at the less refrangible end of the spectrum, the values read on the scale differ from those in the table by not more than ·3 of a unit.

Of the 285 lines given in the tables, all but three or four are found in Schumann's plates. There are, however, a great number of fainter lines in the prismatic spectrum not visible in the plates obtained with the grating. Moreover, owing to the fineness of the slit, and the great dispersion used by Schumann, some of the single lines of the table are seen, by comparison with the prismatic spectrum, to consist of doublets or triplets.

The excellent agreement between these two spectra obtained under such different conditions makes the existence of any chance impurity very improbable.

The extreme limit in Schumann's map has the value λ 1266·9. That author has stated that he obtained some

[1] Lyman, "Astrophysical J.," 23, p. 204, 1906, Plates XII, XIII, XIV; "Memoirs Am. Academy," XIII, No. 3, Plates III, IV, V.

lines too faint to reproduce; from the angles given [1] it is difficult to calculate their exact wave-length, but it seems improbable that they should have a value much below λ 1230, since even thin plates of the best fluorite become opaque at this point. In this connexion it will be remembered that the calculation of Martens from the Kettler-Helmholtz formula for fluorite was not far from this.

This many-line spectrum constitutes the secondary or molecular emission from hydrogen. It has been analysed into systems of bands by Witmer,[2] by Dieke and Hopfield,[3] by Werner,[4] and by Hori.[5] The work of Hori is the most complete and contains measurements of a great number of lines in the hydrogen spectrum. The process of analysis has been assisted by an observation of the author; for though under ordinary circumstances the spectrum presents a great complexity of lines, yet under some conditions it is capable of very striking simplification.[6]

This simplification consists of the intensification of certain groups which always occur in the many-line hydrogen spectrum. The phenomenon occurs when hydrogen is mixed with a great quantity of argon. The details of the effect, as first observed, were as follows :—

If argon containing a trace of hydrogen at a pressure of 2 or 3 mm. is enclosed in a tube with aluminium electrodes, and if no capacity is introduced in the circuit, a characteristic spectrum is obtained. It consists of five groups, each group containing five rather strong lines. These groups begin near λ 1650 and extend to λ 1450. They are all similar in appearance, but they are not all identical in constitution. The distance between the lines in a group is of the order of from one to four Ångström units. If the last trace of hydrogen is removed from the argon, this spectrum disappears. Nitrogen, oxygen, and helium containing a trace of hydrogen and examined in a tube with aluminium electrodes do not produce

[1] "Smithsonian Contributions," 1413, p. 24.
[2] "Phy. Rev.," 28, p. 1223, 1926.
[3] *Ibid.*, 30, p. 400, 1927.
[4] "Proc. Roy. Soc.," 113, p. 107, 1926.
[5] "Zeits. f. Phy.," 44, p. 834, 1927.
[6] Lyman, "Astrophysical J.," 33, p. 105, 1911.

these groups. If the argon and hydrogen are examined in a tube with iron electrodes, the intensity of the groups is very much reduced; if electrodes of copper are employed, the lines are extremely feeble. Under any circumstances, they are destroyed by the introduction of capacity. The most important fact in connexion with these groups is that they are always found in the spectrum of pure hydrogen, no matter how this gas is prepared or what electrodes are employed. Ordinarily they are superposed upon a great number of other lines, but they may be readily distinguished from the rest of the spectrum. All the groups can be identified in the reproductions of spectra published by Schumann; the group which lies between λ 1590 and λ 1600 is the most striking, for at this point of the spectrum it is not obscured by the presence of other strong lines. That these groups are not due to some impurity common to all the electrodes employed was proved by using terminals of very pure silver. The spectrum of hydrogen obtained with these electrodes is identical in every respect with the other spectra of this gas.

The number of these groups has now been considerably extended, and their constitution has been carefully studied; that they belong to the hydrogen molecule there can be no doubt. For further details the reader should consult the article of Hori.[1]

The analysis of the secondary spectrum in the Schumann region not only is of great importance itself, but is also of interest because of its theoretical connexion with the molecular spectrum of the gas in the visible and ultra-violet.

The gap between the end of the secondary spectrum in the ultra-violet and the beginning of the molecular radiations from hydrogen near λ 1675 is filled by a continuous spectrum, this phenomenon was first observed by Schumann; more recently it has been investigated by E. P. Lewis,[2] and by Dieke and Hopfield; [3] it has been utilized by Leifson [4] in his absorption measurements. For a discussion of the theo-

[1] "Zeits. f. Phy.," 44, p. 834, 1927.
[2] "Science," 41, p. 947, 1915.
[3] "Phy. Rev.," 30, p. 416, 1927.
[4] "Astrophysical J.," 63, p. 73, 1926.

retical significance of this spectrum, the reader is referred to a paper by Kaplan.[1]

It is now a well-recognised fact that the primary or atomic spectra of hydrogen may be represented very closely by the formula

$$v = \mathrm{N}\left(\frac{1}{n^2} - \frac{1}{m^2}\right).$$

This relation gives the Paschen series in the red for $n = 3$; the Balmer series for $n = 2$, and a series in the extreme ultra-violet for $n = 1$. With the vacuum grating spectroscope and with a disruptive discharge the author [2] discovered three members of this last series. The first member lies at λ 1215·68; it is a strong and most persistent line which serves as an excellent standard in the region where it occurs. The wave-lengths of this series can be very accurately computed from the formula; they are: λ 1215·68, λ 1025·83, λ 972·54, λ 949·75, λ 937·81, λ 930·75.

All these lines have been observed by Hopfield,[3] by the author, and by other workers.

The author [4] has been able to obtain the first four members of the series reversed by absorption.

Helium.—The spectrum of this gas is represented in the extreme ultra-violet by a principal series, OS — mP, of which seven members have been measured.[5] Under suitable conditions of excitation a region of continuous radiation appears beyond the limit of this series. In addition, there is a line at λ 591·5, which, though of somewhat doubtful origin, is probably due to helium; it may be represented by (OS — 1π). The radiation near λ 600·3 ± ·6 has a band-like character; Sommer [6] has placed it in the band system of the gas.

[1] "Proc. Nat. Acad.," 13, p. 760, 1927.

[2] First edition of this book, p. 78; "Nature," 93, p. 241, 1914.

[3] *Ibid.*, 110, p. 732, 1922.

[4] "Science," 64, p. 89, 1926.

[5] Lyman, "Astrophysical J.," 60, p. 1, 1924; also H. B. Dorgelo and J. H. Abbink, "Zeits. f. Phy.," 37, p. 667, 1926. See Frontispiece.

[6] "Proc. Nat. Acad.," 13, p. 213, 1927.

Ionized helium is represented by two series—[1]

$$v = 4N\left(\frac{1}{2^2} - \frac{1}{m^2}\right) \quad \text{and} \quad v = 4N\left(\frac{1}{1^2} - \frac{1}{m^2}\right).$$

Of the former, the first member is certainly known, the identity of the second and third is still somewhat doubtful. The second series is represented by two members, λ 303·6 and λ 256·3. They form the radiations of the shortest wavelengths in the helium spectrum which have been observed.

The author's determination of the limit of the principal series has made possible an accurate evaluation of the ionization potential of helium. The value is 24·5 volts; this figure may serve as a standard for those who measure critical potentials by the electric method.[2]

Millikan and Bowen are largely responsible for our knowledge of the spectra of the solid elements in the first row of the Periodic Table; their article in the September number of the "Philosophical Magazine," 1927, is not only the source of part of the information to be found in the next few paragraphs, but also contains a Moseley diagram of an interesting type, and an Appendix on the new spectroscopic rules in their relation to the lighter elements.

Beryllium.—The spectra of Be_I and Be_{II} have been studied with the vacuum spark from λ 842 into the visible, by Bowen and Millikan.[3]

Boron.—The spark spectrum between λ 676 and λ 1842 was first investigated by Millikan and Bowen.[4] They have subsequently extended their measurements and identified all the strong lines of B_I, B_{II}, and B_{III}.[5] See also Bowen.[6]

Carbon.—The vacuum spark spectra of this element were first investigated by Millikan and Bowen between λ 369 and λ 1832; [7] Simeon [8] has made measurements on the arc spectrum between λ 370 and λ 2512. Bowen and Ingram [9] give

[1] Lyman, loc. cit. [2] J. Franck, "Zeits. f. Phy.," 11, p. 155, 1922.
[3] "Phy. Rev.," 28, p. 256, 1926. [4] *Ibid.*, 23, p. 7, 1924.
[5] "Proc. Nat. Acad.," 10, p. 199, 1924, and "Phy. Rev.," 26, p. 310, 1925.
[6] *Ibid.*, 29, p. 231, 1927. [7] *Ibid.*, 23, p. 8, 1924.
[8] "Proc. Roy. Soc.," 102, p. 488, 1923, and *ibid.*, 104, p. 368, 1923.
[9] "Phy. Rev.," 28, p. 445, 1926.

a table of wave-lengths which may be regarded as standards in the region between λ 977 and λ 1931. See also Lang.[1] Fowler,[2] and Millikan and Bowen have classified nearly all the strong lines for C_I, C_{II}, C_{III}, and C_{IV}.[3]

Nitrogen.—There exists in the radiation from this substance a molecular or band spectrum, and a number of line spectra due to the atom in various stages of ionization. The bands were first observed by Schumann, and later by the author.[4] Recently Birge and Hopfield [5] have investigated sixty bands between λ 1250 and λ 2025.

The two pairs, λ 1492·8, λ 1494·8, and λ 1742·7, λ 1745·3, which were the first members of the line spectrum discovered by the author, are now attributed to N_I.[6] A table of standard wave-lengths between λ 685 and λ 1747 is given by Bowen and Ingram.[7] Bowen, in a classification of the chief lines of N_{III}, gives values to λ 374.[8] The analysis of the line spectrum has also been carried out by Fowler,[9] by Bowen and Millikan,[10] and by Hopfield.[11] The fine structure of some of the lines has been studied by Bowen and Millikan.[12]

Oxygen.—Schumann [13] states that the spectrum of oxygen "is compounded of three continuous maxima, of which the most refrangible is the strongest. It lies about λ 1850. The observation of these maxima is attended with considerable difficulty on account of their slight photographic efficiency, and because of the bands of oxide of carbon which appear with them." Steubing [14] has investigated the emission of oxygen at the edge of the Schumann region, and has found a

[1] "Phy. Rev.," 28, p. 36, 1926.
[2] "Proc. Roy. Soc.," 105, p. 303, 1924.
[3] "Phil. Mag.," 4, p. 561, 1927; "Phy. Rev.," 26, p. 310, 1925, and *ibid.*, 29, p. 231, 1927.
[4] "Astrophysical J.," 33, p. 98, 1911.
[5] "Phy. Rev.," 29, p. 356, 1927; "Nature," 116, p. 15, 1925.
[6] Fowler, "Proc. Roy. Soc.," 114, p. 663, 1927.
[7] "Phy. Rev.," 28, p. 445, 1926. [8] *Ibid.*, 29, p. 234, 1927.
[9] "Proc. Roy. Soc.," 114, p. 662, 1927.
[10] "Phy. Rev.," 26, p. 150, 1925; *ibid.*, 24, p. 212, 1924.
[11] *Ibid.*, 27, p. 801, 1926. [12] "Phil. Mag.," 48, p. 259, 1924.
[13] "Smithsonian Contributions," 1413, p. 16.
[14] "Ann. d. Phy.," 33, p. 553, 1910.

series of lines or bands identical with those which he attributed to the fluorescence of the gas. He believes that these sharp emission lines are related to the continuous maxima mentioned by Schumann.

For a statement of the modern view of the band systems of oxygen in the ultra-violet, the reader will do well to consult a paper by Hopfield.[1]

The first definite information of the line spectrum of this element is due to Hopfield;[2] Millikan and Bowen,[3] in their work with the vacuum spark, observed lines common to many elements; these they attributed to oxygen; their table extends from λ 136 to λ 1338. Carroll[4] and Bowen and Ingram[5] give a table of standard wave-lengths between λ 507 and λ 835. Bowen,[6] in the course of the study of the series relations in oxygen, carries the spectrum of O_{III} to λ 328.[7] Hopfield has made important contributions[8] to our knowledge of the structure of the spectrum.[9]

Fowler has recently contributed an interesting note on the light thrown on the origin of the spectrum of "Nebulium" by the structure of the oxygen spectrum in the extreme ultra-violet.[10]

Fluorine.—The spark spectrum was first measured by Millikan and Bowen[11] from λ 378 to λ 1143. A more detailed study of the spectra of this element in various stages of ionization has been made by Bowen.[12]

Neon.—The spectrum has been studied by Lyman and Saunders,[13] and by Dorgelo and Abbink.[14] Its most prominent

[1] "Phy. Rev.," 29, p. 79, 1927. [2] "Science," 54, p. 553, 1921.
[3] "Phy Rev.," 23, p. 1, 1924.
[4] "Trans. Roy. Soc. Lond.," 225, p. 357, 1926.
[5] "Phy. Rev.," 28, p. 445, 1926. [6] *Ibid.*, 29, p. 231, 1927.
[7] See also Fowler, "Proc. Roy. Soc.," 117, p. 317, 1928.
[8] "Astrophysical J.," 59, p. 114, 1924.
[9] See also Bowen and Millikan, "Phy. Rev.," 27, p. 144, 1926; "Nature," 118, p. 410, 1926; and "Phil. Mag.," 48, p. 259, 1924.
[10] "Nature," 120, p. 582, 1927.
[11] "Phy. Rev.," 23, p. 11, 1924.
[12] "*Ibid.*, 29, p. 244, 1927; see also "Phil. Mag.," 48, p. 259, 1924
[13] "Proc. Nat. Acad. Sci.," 12, p. 92, 1926
[14] "Zeitsch. f. Phy.," 37, p. 667, 1926.

feature is the strong pair at λ 735·9 and λ 743·7. The ionization potential is 21·47 volts, which corresponds to λ 574·9 as the limit of the principal series. Judging from Dorgelo's observations on argon, krypton, and xenon (*q.v.*), it is to be expected that absorption begins on the short wave-length side of this point in the spectrum.

Sodium.—Millikan and Bowen have investigated the spectrum of this substance with the vacuum spark.[1] Between λ 300 and λ 2000 they find but two faint lines, lying at λ 372·3 and λ 376·6.

Magnesium.—The spark spectrum was first systematically investigated with a vacuum grating spectroscope by the author; the source being placed in hydrogen at atmospheric pressure.[2] Two pairs were discovered with a separation of $1/\lambda = 90$; they lie at λ 1735·0 and λ 1737·8, and at λ 1750·9 and λ 1753·6. There is also, perhaps, a single line at 1828·1. The pairs have been observed by Millikan and Bowen; [3] they also give three lines at the extreme limit of the region: λ 231·6, λ 320·9, and λ 323·2; the first two of which they describe as the L doublet of magnesium. The existence of these radiations has been confirmed by the writer. The values formerly obtained by Handke with a fluorite prism spectroscope and a spark in air [4] do not agree with the data obtained by other workers. See also McLennan, Young, and Ireton.[5] The author has [6] succeeded in obtaining some additional lines by the use of an arc in high vacuum operated by a trembler device taking 10 amperes at 40 volts. They are to be attributed to Mg_{II}, and form members of the $(1\sigma - m\text{II})$ series; [7] they occur at λ 1240·1, λ 1240·5, λ 1025·9, and λ 946·6.

Aluminium.—As the pioneer investigations of the spark spectrum of this substance possess some interest from the historic point of view, a few paragraphs will be devoted to them.

[1] "Phy. Rev.," 23, p. 11, 1924.
[2] "Astrophysical J.," 35, p. 341, 1912.
[3] "Phy. Rev.," 23, p. 12, 1924.
[4] "Berlin Inaug. Dis," 1909.
[5] "Proc. Roy. Soc.," 98, p. 102, 1920.
[6] "Science," 60, p. 388, 1924.
[7] Fowler, "Series in Line Spectra," p. 120.

Very early in his researches Schumann [1] studied the spark spectra of a great number of metals, but he gave no wave-lengths for the lines he discovered, and his apparatus, which at that time was crude, did not permit him to follow the investigation much beyond the limit attained by Stokes. Later, when he had perfected his spectroscope, he returned to the subject. Some of his results for cadmium and for aluminium are shown in Plate II, vol. 102, II*a*, p. 694, "Proceedings of the Vienna Academy." The most refrangible of the rays there represented has a value λ 1670. The study of all spark spectra in the extreme ultra-violet is beset by an obvious difficulty, for the layer of air which surrounds the spark absorbs the light energetically before it can enter the vacuum apparatus. Schumann attempted to surmount this difficulty by producing the spark in hydrogen.[2] His first attempts were not very successful, probably because he tried to work with the hydrogen at low pressures, a procedure which greatly weakens metallic lines. He soon abandoned the spark as a source of light and turned his attention to the discharge tube with which he succeeded in obtaining such brilliant results. Had not illness overtaken him, he would doubtless have returned to the subject of the emission of solids.

The early work at Harvard added hardly anything to the knowledge of spark spectra, for the extension of the hydrogen spectrum and the measurement of its lines fully occupied the attention of the observer. Handke,[3] in Berlin, was the first to make systematic measurements. Using a vacuum prism spectroscope of the Schumann type, he attached to it a vacuum tube of the form used at Harvard. This tube was filled with hydrogen and served to produce a standard spectrum. The spark was formed in air in such a way that the light passed through the discharge tube before entering the spectroscope. Thus the extent of the spectra was limited by the absorption of the layer of air between the spark and the window of the discharge tube. His most refrangible line lies at λ 1594. All his results rest on the measurements of the

[1] "Ber. Akad. Wis. Wien.," 102, II*a*, p. 438. [2] *Ibid.*
[3] "Berlin Inaug. Dis.," 1909.

hydrogen spectrum. He studied the spectra of Al, Cu, Au, Ag, Sn, Zn, Mg, and Hg.

The next work in the emission of solids was done with the vacuum grating spectroscope in order to verify certain predictions as to the construction of the spectra of the alkali earths.[1] The method adopted was a distinct improvement over the procedure of the earlier investigators, in that, by placing the spark in hydrogen at atmospheric pressure, the absorption of the air was removed, and it thus became possible to follow spark spectra much farther into the extreme ultra-violet than had been possible before. The most refrangible line obtained by this method had the value λ 1238, a position very close to the limit set by the fluorite window which it was necessary to employ.

Aluminium was chosen as the first substance for investigation because its spectrum had been studied by Handke, and it therefore afforded opportunity for comparing the grating measurements with measurements obtained by another type of instrument. The greater light-intensity of the prism instrument in the region of wave-lengths less refrangible than λ 1600 was shown by the fact that some faint lines were given by Handke which were not easily observed with the grating. On the other hand, the result of the elimination of the absorption of the fluorite prism and lenses and of the air near the spark was illustrated by the fact that the lines of shorter wave-length than λ 1600 measured with the grating were not discovered in the earlier work.

An inspection of the aluminium spark spectrum from the grating shows that the well-known pair at λ 1862, λ 1854 are by far the strongest lines in the field. The other lines decrease in intensity with decrease in wave-length.

After the work with the spark in hydrogen was completed, an investigation by Lenard [2] on volume ionization renewed the interest in the nature of the aluminium spark in air. It has been shown that the ability to produce volume ionization by

[1] Lyman, "Astrophysical J.," 35, p. 341, 1912.

[2] Lenard and Ramsauer, "Sitz. Heidelberg Akad. d. Wiss. Abhand.," 31, 1910.

light increases in the Schumann region with decrease in wave-length; in fact, some investigators go so far as to assert that the phenomenon occurs only when light on the more refrangible side of λ 1400 is employed. Now Lenard obtained very strong ionization when he used a very powerful spark between aluminium terminals, and his results indicated that the effective light lay in the extreme Schumann region. On consulting the data for the aluminium spark in hydrogen, it was obvious that no strong lines existed in the extreme ultra-violet. Unless, therefore, lines were to be found in the spectrum of the aluminium spark in air which were not present with the spark in hydrogen, Lenard's results could not easily be explained. New experiments were accordingly undertaken with the grating spectroscope;[1] they yielded more interesting results than any of the previous attempts of this character. Their success was due to the fact that the pointed spark terminals were placed nearly in contact with the window of the spectroscope, so that the spark played against the surface of the fluorite. An exposure of six minutes destroyed the fluorite window, but a strong spectrum was registered on the photographic plate. Between λ 1400 and λ 1900 the lines of this spectrum are the same as those observed when the spark was in hydrogen; but there is a distinct difference in the distribution of intensities in the two spectra in this region, owing to the selective nature of the absorption of the air and to the difference in intensity of certain "air lines." Near λ 1300, with the spark in air, there is a group of strong lines not observed with the aluminium spark in hydrogen. It is to this group that the ionization effects observed by Lenard may perhaps be attributed. All the lines in the region of λ 1300 cannot be assigned to the same cause. Those at λ 1302·0, λ 1304·8, λ 1305·8, λ 1334·6, and λ 1335·7 are due to oxygen and carbon. The lines λ 1275·0, λ 1276·4, λ 1310·8, λ 1319·4 were provisionally placed under aluminium; they are due to nitrogen. It must be remarked that Lenard found several metals produced nearly the same ionizing effects when used

[1] Lyman, "Physik. Zeitsch.," 13, p. 583, 1912.

as spark terminals, a result which would indicate that all the effective rays were not produced by the metals themselves.

The vacuum spark spectrum of aluminium has been studied by Millikan and Bowen,[1] from λ 160 to λ 1862. Hutchinson has measured wave-lengths both in the arc and in the spark spectrum;[2] some of the lines which he tabulates are evidently due to impurities. Sawyer and Paschen[3] have made an exhaustive study of the spark spectrum of Al_{II}, using a hollow cylindrical cathode in helium as source. They give a table, containing a wealth of lines, covering the region between λ 933 and λ 2049.

The writer has added a few members to the spectrum of Al_{III}[4] by the use of the vacuum spark; they lie at λ 891·9 and λ 893·8 ($3p - md$); λ 855·0; λ 856·7 and λ 725·7; λ 726·7 ($3p - ms$); λ 696·0 and λ 560·3, λ 511·1 ($3s - mp$).

McLennan, Young and Ireton[5] have measured the spectrum from a spark in helium.

Silicon.—For a complete discussion of the spectrum of this substance in successive stages of ionization the reader should consult Fowler;[6] he should compare Millikan and Bowen,[7] and McLennan and Shaver.[8] The spark spectrum extends to the neighbourhood of λ 360.

Phosphorus.—The vacuum spark was first investigated by Millikan and Bowen[9] between λ 824 and λ 1646. More recently the same authors have treated the spectrum of this element in successive stages of ionization.[10] The first of these references relates to a paper containing an interesting study of the similarity of "stripped atom" spectra of the elements in the periodic tables between sodium and chlorine. The arc

[1] "Phy. Rev.," 23, p. 1, 1924.
[2] "Astrophysical J.," 58, p. 280, 1923.
[3] "Ann. d. Phy.," 84, p. 1, 1927.
[4] "Science," 60, p. 388, 1924.
[5] "Proc. Roy. Soc.," 98, p. 95, 1920.
[6] "Trans. Roy. Soc. Lond.," 225, p. 1, 1924.
[7] "Phy. Rev.," 23, p. 1, 1924.
[8] "Trans. Roy. Soc. Canada," 18, p. 1, 1924.
[9] "Phy. Rev.," 23, p. 1, 1924.
[10] "Phy. Rev.," 25, pp. 295, 591; and *ibid.*, p. 600, 1925; and 29, p. 510, 1927; and 31, p. 34, 1928.

spectrum has been studied by Saltmarsh between λ 2555 and λ 1671.[1]

Sulphur.—Information as to the spectrum of this substance will be found in the first four papers of Millikan and of Bowen as cited under phosphorus. There are a considerable number of lines listed in the first paper [2] which have not been classified. Two multiplets in the spectrum of sulphur are given by Hopfield,[3] their shortest wave-lengths are λ 1381·6 and λ 1473·0 respectively.

Chlorine.—Most of the investigation of the vacuum spark spectrum of this substance has been done by Millikan and Bowen; the first four references to the work of these authors under phosphorus cover the subject. The reader will be interested to compare two brief notes of Hopfield [4] relating to the vacuum tube spectrum of this element. Turner [5] has studied the spectra obtained by passing a continuous current through hydrogen chloride gas and through carbon tetrachloride; he finds seven strong lines which he attributes to chlorine. See also Vaudet.[6]

Argon.—The two strong resonance lines of this gas were discovered by the author and Professor Saunders; [7] they lie at λ 1048·26 and λ 1066·70. The structure of the whole spectrum has been studied by Saunders [8] and by Meissner.[9] Dorgelo and Abbink [10] have made a careful study, both experimental and theoretical, of the spectrum of argon in the extreme ultra-violet. The reader will find a list of wave-lengths in the region between λ 500 and λ 1100 in this valuable paper.

Potassium.—Millikan and Bowen have measured the vacuum spark spectrum of this element between λ 312 and

[1] "Phil. Mag.," 47, p. 874, 1924.

[2] "Phy. Rev.," 23, p. 1, 1924. [3] *Ibid.*, 26, p. 282, 1925.

[4] *Ibid.*, 23, p. 766, 1924; and *ibid.*, 26, p. 282, 1925.

[5] *Ibid.*, 27, p. 397, 1926. [6] "Comptes Rendus," 185, p. 1270, 1927.

[7] "Nature," 116, p. 358, 1925; see also Hertz and J. H. Abbink, "Die Naturwissenschaften," 14, p. 648, 1926.

[8] "Proc. Nat. Acad. Sci.," 12, p. 556, 1926; and *ibid.*, 13, p. 596, 1927.

[9] "Zeitsch. f. Physik.," 37, p. 238, 1926; *ibid.*, 39, p. 172, 1926; *ibid.*, 40, p. 839, 1927.

[10] *Ibid.*, 41, p. 753, 1927.

λ 1303·6.[1] Shaver [2] has observed, through fluorite, the spectrum between λ 1602 and λ 1895. Hopfield, in a brief note,[3] calls attention to certain multiplets among the radiations from potassium.

Calcium.—The first investigation of the spectrum of this element was made by the author.[4] The source was a spark in hydrogen at atmospheric pressure. The region examined extended from λ 1872 to the limit set by the absorption of fluorite, λ 1246. Four pairs were discovered with the separation required by theory, wave-number $1/\lambda = 223$; three pairs were also found with a separation $1/\lambda = 70$. More recently Lang [5] has investigated the spectrum of the vacuum spark, using a grating of 6 feet radius with 30,000 lines to the inch; the dispersion which he employed was considerably greater than that of other observers. Millikan and Bowen [6] have also worked with the vacuum spark; their measurements extend from λ 269 to λ 1838·9. McLennan, Young, and Ireton [7] have investigated the arc spectrum between λ 1553 and λ 2209. For the structure of the spectrum the reader may well consult Russell and Saunders.[8]

That the agreement between the observations of all these investigators is not perfectly satisfactory may be attributed partly to differences in the character of the sources employed, partly to the character of the lines.

Scandium.—The vacuum spark spectrum of this element has been measured by Ireton [9] between λ 507 and λ 2230.

Titanium and Vanadium.—The spectra of these elements have been studied by Lang.[10] The spectra of doubly and trebly ionized titanium have been analysed by Russell and Lang.[11]

[1] "Phy. Rev.," 23, p. 21, 1924.
[2] "Trans. Roy. Soc. Canada," 18, p. 27, 1924.
[3] "Phy. Rev.," 27, p. 638, 1926.
[4] "Astrophysical J.," 35, p. 341, 1912.
[5] *Ibid.*, 64, p. 167, 1926.
[6] "Phy. Rev.," 23, p. 1, 1924.
[7] "Proc. Roy. Soc.," 98, p. 95, 1920.
[8] "Astrophysical J.," 62, p. 1, 1925.
[9] "Trans. Roy. Soc. Canada," 18, p. 103, 1924.
[10] "Trans. Roy. Soc. Lond." Vol. 224, p. 371, 1924.
[11] "Astrophysical J.," 66, p. 13, 1927.

Chromium.—Millikan and Bowen [1] have measured the spectrum of the vacuum spark of this substance between λ 877 and λ 2025. Lang [2] has used the same source; he gives a list of wave-lengths between λ 400 and λ 1900. L. and E. Bloch [3] have studied the spectrum produced by a spark in nitrogen, using a fluorite prism instrument. The range of their observations lies between λ 1505 and λ 1926. They state that their results do not agree with those of Lang.

Manganese.—L. and E. Bloch [4] give a long list of wave-lengths for this substance between λ 1464 and λ 1868. Lang's values [5] extend from λ 310 to λ 2028. The two sets of measurements are not in agreement.

McLennan, Cohen, and Liggett [6] give some measurements of lines absorbed by manganese vapour.

Iron.—The spark spectrum of this element has been measured between λ 1505 and λ 1895 by L. and E. Bloch.[7] The vacuum spark has been studied by Millikan, Bowen, and Sawyer [8] between λ 270 and λ 2153.

McLennan and his students [9] made some observations on the arc spectrum.

McLennan and McLay [10] have studied the absorption of iron vapour.

Cobalt.—The spark spectrum has been investigated by L. and E. Bloch,[11] and by Lang.[12] The observations of the latter extend from λ 342 to λ 2097. The arc spectrum has been studied by McLennan and his students [13] between λ 1670 and λ 2140.

Measurements of the absorption of cobalt vapour have been made by McLennan and Cooley.[14]

[1] "Phy. Rev.," 23, p. 1, 1924.
[2] "Trans. Roy. Soc. Lond.," 224, p. 371, 1924.
[3] "Journal d. Phy.," 6, p. 105, and p. 154, 1925.
[4] Loc. cit.
[5] Loc. cit.
[6] "Trans. Roy. Soc. Canada," 20, p. 365, 1926.
[7] Loc. cit.
[8] "Astrophysical J.," 53, p. 150, 1921.
[9] "Proc. Roy. Soc.," 95, p. 258; and p. 316, 1919.
[10] "Trans. Roy. Soc. Canada," 19, p. 89, 1925.
[11] Loc. cit.
[12] "Trans. Roy. Soc. Lond.," 224, p. 371, 1924.
[13] Loc. cit., p. 316.
[14] "Trans. Roy. Soc. Canada," 20, p. 349, 1926.

Nickel.—The spark spectrum has been studied by L. and E. Bloch,[1] and by Millikan, Bowen, and Sawyer;[2] the measurements of the latter observers extend from λ 731 to λ 1860. McLennan and his students[3] give wave-lengths between λ 1650 and λ 2005 in the arc spectrum. The absorption spectrum of nickel vapour has been studied by McLennan and Cooley.[4]

Copper.—The spectrum of the vacuum spark has been studied by Millikan and Bowen[5] from λ 155 to λ 900. L. and E. Bloch[6] give wave-lengths for the spark in nitrogen from λ 1358 to λ 1930. McLennan, Young, and Ireton[7] have investigated the arc spectrum from λ 1216 to λ 2000. McLennan and McLay[8] have studied the absorption in copper vapour, but only on the less refrangible side of λ 2000.

Zinc.—The arc spectrum of this metal affords an early example of the manner in which series relations observed among lines of an element may be used to check wave-length determinations in the extreme ultra-violet.

Paschen[9] has shown that certain lines in the spectra of zinc, cadmium, and mercury may be arranged to form Principal Series given by formulæ of a type which has become standard in series spectra investigations. The lines lie in a well-known region and their wave-lengths have been determined with precision; from these measurements it has been possible to calculate accurately the constants which enter into the formulæ in question. Paschen[10] pointed out that the change of one parameter in these formulæ, in a manner justified by analogy with other similar relations, would yield Principal Series whose members occurred in the Schumann region. Inspired by this prediction, Wolff[11] has studied the arc spectra of zinc, cadmium, and mercury by means of a prism vacuum spectroscope of the same general design as that used by Schumann.

[1] Loc. cit. [2] Loc. cit. [3] Loc. cit., p. 316.
[4] Loc. cit. [5] "Phy. Rev.," 23, p. 1, 1924.
[6] Loc. cit. [7] "Proc. Roy. Soc.," 98, p. 105, 1920.
[8] "Trans. Roy. Soc. Canada," 19, p. 89, 1925.
[9] "Ann. d. Phy.," 35, p. 860, 1911; 40, p. 602, 1913.
[10] Loc. cit. [11] "Ann. d. Phy.," 42, p. 825, 1913.

It is obvious that the arc must be formed either in vacuo or in some transparent gas; the first alternative was chosen by Wolff. The chief experimental difficulty which besets the use of the arc at reduced pressures is the formation of metallic films on the window which separates the arc chamber from the body of the spectroscope; this difficulty is particularly acute when the extreme ultra-violet is the region to be investigated. Wolff overcame the difficulty by employing a modification of the quartz amalgam lamp first described by Stark.[1] The formation of the film was prevented by the application of a cooling chamber to that part of the lamp which lay between the arc and the window. An arrangement was also introduced whereby the hydrogen spectrum could be superposed upon that of the metal under investigation. This lamp served for the study of cadmium and zinc; in the case of mercury, a lamp of somewhat different shape was used; it was entirely immersed in a cooling bath.

The wave-length measurements were referred to the aluminium lines in the region from λ 1990 to λ 1854 as given by Runge, and Eder and Valenta; from there on to λ 1670 they rested on the values of aluminium spark spectrum as determined at Harvard. On the more refrangible side of this point, the values for the hydrogen spectrum were taken as standards.

The values given by Wolff confirm the predictions of Paschen to a high degree of accuracy, as may be seen from the following tables:—

Zinc: Principal Series. Single Lines (1·5 S — mP).

m	3	4	5	6
λ calculated	1589·64	1457·64	1404·18	1376·97
λ observed	1589·76	1457·56	1404·19	1376·87
Diff.	0·12	0·08	0·01	0·1

Cadmium: Principal Series. Single Lines (1·5 S — mP).

m	3	4	5	6	7
λ calculated	1669·30	1526·73	1469·35	1440·15	1423·22
λ observed	1669·29	1526·85	1469·39	1440·18	1423·23
Diff.	0·01	0·12	·04	·03	·01

[1] "Physik. Zeitsch.," 6, p. 438, 1905.

Mercury : Principal Series. Single Lines (1·5 S — mP).

m	2	3
λ calculated	1849·6	1402·71
λ observed	1849·57	1402·72
Diff.	·03	·01

These calculated values may be taken as wave-length standards in the spectra of the three elements.

Besides the members of these three Principal Series, there is also a Combination Series in each of the three metals : one term of such an arrangement has been found for zinc, two for cadmium, and one for mercury.

So confident is Wolff of the accuracy of values derived from Paschen's formulæ that he applies a correction to the hydrogen wave-lengths by comparing his wave-lengths, as determined from hydrogen, with the calculated values which he assumes correct.

The maximum correction applied to my table in this way is 0·12 unit, a value rather too flattering to the accuracy of the measurements of the hydrogen spectrum, since the wave-lengths claim an accuracy of only 0·2 of a unit at best.

The arc spectrum has been more recently measured by McLennan, Ainslie, and Fuller [1] between λ 1445 and λ 2000. The spectrum of the spark in hydrogen has been tabulated by L. and E. Bloch [2] between about the same limits. The most complete list of wave-lengths is due to Sawyer ; [3] he employed a vacuum spark ; the range covered extends from λ 316 to λ 2140. Wood [4] has obtained plates of the zinc spectrum of great excellence, but some of the lines in his tables may well be due to impurities. The best wave-length determinations which we have are due to Laporte and Lang ; [5] they relate entirely to doubly-ionized zinc.

Gallium.—The spectrum of the vacuum spark has been measured by Carroll [6] from λ 600 to λ 5000. For the spectrum

[1] " Proc. Roy. Soc.," 95, p. 316, 1919.
[2] " Journal de Phy.," 2, p. 229, 1921.
[3] " Astrophysical J.," 52, p. 286, 1920.
[4] " Phil. Mag.," 46, p. 741, 1923.
[5] " Phy. Rev.," 30, p. 378, 1927.
[6] " Trans. Roy. Soc. Lond.," 225, p. 357, 1925.

of Ga_{II} and Ga_{III} see Lang.[1] Weinberg[2] tabulates lines in this substance to λ 124. The reality of lines of such very short wave-lengths is open to grave doubt.

Germanium.—The most complete list of the lines in the spectrum from the vacuum spark is given by Carroll;[3] it extends from λ 746 to λ 1625. Ireton[4] gives a shorter table, but covering the wider range, λ 319 to λ 2256. Lang[5] has studied the spectrum of Ge_{III} and Ge_{IV}.

Arsenic.—The spectrum from the spark in hydrogen at atmospheric pressure was first measured by L. and E. Bloch.[6] The vacuum spark spectrum has been measured by Lang;[7] there is a singular lack of agreement between the results of these two observers. McLennan and McLay have investigated the absorption of arsenic vapour to λ 1600.[8]

Selenium.—The arc spectrum has been measured to λ 1430 by McLennan, Young, and Ireton.[9]

Bromine.—The arc spectrum has been measured by Turner[10] between λ 1230 and λ 2050. Vaudet[11] gives a long list of lines extending from λ 1300 to λ 2246. He employed a tube without electrodes, containing a little sodium bromide and excited by a high frequency discharge.

Krypton.—Taylor has published a preliminary note on the radiations from this element.[12] The resonance lines occur at λ 1164·90 and λ 1235·87.

Abbink and Dorgelo have made a careful study of the spectrum[13] under various conditions of discharge from λ 500 to λ 1500. Some of the lines given by Taylor they attribute to xenon. For the ionizing potential they find 13·9 volts. As they have already observed in the case of argon, certain

[1] "Phy. Rev.," 30, p. 762, 1927.
[2] "Proc. Roy. Soc.," 107, p. 138, 1925.
[3] Loc. cit.
[4] "Trans. Roy. Soc. Canada," 18, p. 103, 1924.
[5] Loc. cit.
[6] "Journal de Phy.," 2, p. 229, 1921.
[7] Loc. cit.
[8] "Trans. Roy. Soc. Canada," 19, p. 89, 1925.
[9] "Proc. Roy. Soc.," 98, p. 95, 1920.
[10] "Phy. Rev.," 27, p. 397, 1926.
[11] "Comptes Rendus," 185, p. 1270, 1927.
[12] "Proc. Nat. Acad. Sci.," 12, p. 658, 1926.
[13] "Zeitsch. für Physik," 47, p. 221, 1928.

lines lying on the short wave-length side of the limit of the series are absorbed as the pressure of krypton is increased.

Rubidium.—W. W. Shaver [1] has studied the spectrum of the electrodeless discharge between λ 1717 and λ 2300.

Strontium.—The only observations on the spectrum of this substance were made by the author [2] some time ago. A spark in hydrogen was used as source. The computations of Saunders [3] show that the limits of the subordinate series lie in the neighbourhood of λ 1700; it is a recognized property of these series that the members rapidly decrease in intensity as they near the limit. It is not surprising, therefore, that only one pair with the required separation, $1/\lambda = 800$, in the Schumann region has been observed. The position is λ 1847 and λ 1820. There are, however, two striking pairs, with the predicted separation, $1/\lambda = 285$.

These three pairs constitute the spectrum of strontium; the other lines which occur on the plate are chiefly due to calcium and aluminium.

Yttrium.—Bowen and Millikan have measured the spectrum of Y_{III},[4] using the vacuum spark. With a spark in helium, McLennan and Liggett [5] find but one line at λ 1787·64 in the region bounded by the absorption of fluorite. There are some measurements on both the arc and spark in the region between λ 1900 and λ 2300, by McDonald, Sutton, and McLay.[6]

Zirconium.—Radiations belonging to Zr_{IV} have been investigated by Bowen and Millikan.[7] The general spectrum has also been measured by McDonald, Sutton, and McLay [8] to λ 1866, and by McLennan and Lewis [9] to λ 1656 for the spark in helium.

Niobium.—The arc and spark spectrum have been measured by McLennan and Liggett.[10] They give a considerable number of lines between λ 1580 and λ 2300.

[1] "Trans. Roy. Soc. Canada," 18, p. 23, 1924.
[2] "Astrophysical J.," 35, p. 341, 1912. [3] *Ibid.*, 32, p. 165, 1910.
[4] "Phy. Rev.," 28, p. 923, 1926.
[5] "Trans. Roy. Soc. Canada," 20, p. 377, 1926.
[6] *Ibid.*, p. 313, 1926. [7] Loc. cit. [8] Loc. cit.
[9] "Proc. Roy. Soc.," 98, p. 109, 1920. [10] Loc. cit.

Molybdenum.—The spectrum of the vacuum spark has been measured by Lang [1] from λ 373 to λ 1997. See also McLennan and Lewis.[2]

Palladium.—A discussion of the structure of the spectrum, together with tables of emission and absorption lines, are to be found in a paper by McLennan and Smith.[3] See also McLennan, Cohen, and Liggett.[4]

Silver.—L. and E. Bloch [5] have measured the spectrum from the spark in nitrogen from λ 1389 to λ 1890. McLennan, Young, and Ireton [6] gave wave-lengths for the arc to λ 1540.

Cadmium.—The early measurements by Wolff have already been mentioned under zinc. His lines: 1669·30, 1526·73, 1469·35, 1440·15, 1423·22 may be regarded as standards in the arc spectrum of this substance. The spectrum of the spark in hydrogen has been measured to λ 1415 by L. and E. Bloch.[7] Lang [8] has followed the vacuum spark spectrum to λ 370.

Indium.—Carroll [9] has measured the spectrum of the vacuum spark, and has studied its structure. Lang [10] gives wave-lengths for singly- and doubly-ionized indium.

The measurements of Weinberg,[11] though they cover a wide range, are not in good agreement with the results of other observers.

Tin.—The spectrum of the spark in hydrogen at atmospheric pressure has been measured by L. and E. Bloch [12] to the limit set by the transparency of fluorite.

Carroll [13] gives wave-lengths for the vacuum spark, based on a correction curve resting on the values of Bloch; they

[1] "Trans. Roy. Soc. Lond.," 224, p. 371, 1924. [2] Loc. cit.
[3] "Proc. Roy. Soc.," 112, p. 110, 1926.
[4] "Trans. Roy. Soc. Canada," 20, p. 365, 1926.
[5] "Journal de Phy.," 6, p. 154, 1925.
[6] "Proc. Roy. Soc.," 98, p. 95, 1920.
[7] "Journal de Phy.," 2, p. 245, 1921. [8] Loc. cit.
[9] "Trans. Roy. Soc. Lond.," 225, p. 357, 1925.
[10] "Proc. Nat. Acad. Sci.," 13, p. 341, 1927; and "Phy. Rev.," 30, p. 762, 1927.
[11] "Proc. Roy. Soc.," 107, p. 138, 1925.
[12] "Comptes Rendus," 177, p. 1025, 1923. [13] Loc. cit.

extend from λ 1300 to λ 1950. Lang [1] gives a list of lines extending from λ 390 to λ 2040; in a subsequent publication [2] he discusses the structure of the spectrum of Sn_{IV}. McLennan, Ainslie, and Fuller [3] have measured the arc spectrum between λ 1400 and λ 2150. McLennan, Young, and McLay [4] have treated the absorption and series spectra of tin.

Antimony.—The spectrum of the spark in a hydrogen atmosphere has been measured by L. and E. Bloch.[5] Wave-lengths for the vacuum spark are given by Lang [6] from λ 456 to λ 2086. In a subsequent paper [7] he isolates the lines belonging to Sb.v. The spectrum of the arc in vacuum has been measured by McLennan, Young, and Ireton [8] between λ 1437 and λ 1931. McLennan and McLay [9] give four wave-lengths, λ 1525·2, λ 1514·1, λ 1483·5, and λ 1481·0, as absorbed by the vapour of antimony.

Tellurium.—Lang [10] gives lines in the vacuum spark spectrum from λ 509 to λ 2049. McLennan and Lewis [11] have measured the spectrum from the spark in helium to λ 1634. The agreement between values obtained in these two investigations is not very satisfactory. McLennan and Cooley [12] give eleven lines absorbed by tellurium vapour between λ 1659 and λ 1998.

Iodine.—Turner [13] gives a table of wave-lengths of lines produced by a discharge tube excited in a number of ways. The region covered extends from λ 1234 to λ 2062, being limited by the transparency of a fluorite window.

[1] "Trans. Roy. Soc. Lond.," 224, p. 371, 1924.
[2] "Proc. Nat. Acad. Sci.," 13, p. 341, 1927.
[3] "Proc. Roy. Soc.," 95, p. 316, 1919.
[4] "Trans. Roy. Soc. Canada," 18, p. 57, 1924.
[5] "Journal de Phy.," 2, p. 229, 1921; and "Comptes Rendus," 178, p. 472, 1924.
[6] "Trans. Roy. Soc.," 224, p. 371, 1924.
[7] "Proc. Nat. Acad. Sci.," 13, p. 341, 1927.
[8] "Proc. Roy. Soc.," 98, p. 95, 1920.
[9] "Trans. Roy. Soc. Canada," 19, p. 89, 1925.
[10] "Trans. Roy. Soc. Lond.," 224, p. 371, 1924.
[11] "Proc. Roy. Soc.," 98, p. 109, 1920.
[12] "Trans. Roy. Soc. Canada," 20, p. 349, 1926.
[13] "Phy. Rev.," 27, p. 397, 1926.

Xenon.—The spectrum has been investigated by Abbink and Dorgelo [1] between λ 635 and λ 1500. They give the ionization potential as 12 volts. Absorption sets in beyond the ultra-violet limit of the principal series near λ 1029.

Cæsium.—This element possesses a spectrum very rich in lines between λ 1669 and λ 2300, as has been shown by Shaver [2] in his study of the emission from the electrodeless discharge.

Barium.—The state of our knowledge of the spectrum of this substance is by no means satisfactory. The author [3] made measurements of wave-lengths obtained from a spark in helium, but it is by no means certain that the lines he observed belong to the element in question.

Lanthanum. — McDonald, Sutton, and McLay [4] have measured the arc and spark spectra from λ 1874 to λ 2256. McLennan and Liggett [5] have followed the spectrum to λ 1699. They can find no spark lines in the region limited by fluorite, and but four lines belonging to the arc.

Cerium.—The references are the same as for lanthanum.

Praseodymium.—See McLennan and Liggett.[6]

Neodymium.—McDonald, Sutton, and McLay ; [7] McLennan and Liggett [8] find but one line in the spark λ 1625·50.

Tungsten.—The spark spectrum has been measured by L. and E. Bloch [9] between λ 1453 and λ 1877.

Platinum.—The spectrum from a spark in an atmosphere of nitrogen has been measured by L. and E. Bloch [10] between λ 1330 and λ 1911. Lang [11] has used a vacuum spark; the range covered extends from λ 390 to λ 2014. His measurements do not agree satisfactorily with those of the Blochs. McLennan, Cohen, and Liggett [12] give a considerable number of wave-lengths absorbed by platinum vapour.

[1] " Zeitsch. für Physik," 47, p. 221, 1928.
[2] " Trans. Roy. Soc. Canada," 18, p. 23, 1924.
[3] " Astrophysical J.," 35, p. 341, 1912.
[4] " Trans. Roy. Soc. Canada," 20, p. 313, 1926.
[5] *Ibid.*, p. 377, 1926.
[6] Loc. cit.
[7] Loc. cit.
[8] Loc. cit.
[9] " Journal de Phy.," 6, p. 105 ; and p. 154, 1925.
[10] Loc. cit., p. 154.
[11] " Trans. Roy. Soc. Lond.," 224, p. 371, 1924.
[12] " Trans. Roy. Soc. Canada," 20, p. 365, 1926.

Gold.—The spectrum of the spark in nitrogen has been measured by L. and E. Bloch [1] between λ 1341 and λ 1919, and by Lang [2] to λ 458, using the vacuum spark. The arc spectrum from λ 1552 to λ 2000 has been measured by McLennan and Liggett; [3] they have taken the spark wavelengths as determined by the Blochs as standards. The structure of the arc spectrum has been investigated by McLennan and McLay.[4] The same authors [5] give six lines between λ 1646 and λ 2675, which they observe to be absorbed by gold vapour.

Mercury.—The following lines have been observed by the author [6] in the arc spectrum: 1402·5, 1518·6, 1649·8, 1774·9, 1810 (band), 1832·6, 1849·6. Wolff [7] gives 1402·71 and 1849·6 as standards.

Two forms of mercury arc were employed. In one, the whole vessel was of quartz, and the light entered the spectroscope through the side of the lamp. In the other, the vessel was of glass, fitted with a fluorite window. The spectrum is dominated by the broad unsymmetrical line at λ 1849·6, which considerably exceeds in strength any single line in this region in the spectrum of any substance heretofore examined. The line is easily reversed, a fact which has already been noted by Tian.[8] The other six lines which go to make up the arc spectrum in the region limited by the transparency of fluorite, though much inferior in intensity, are still fairly strong.

The relation between the arc and the spark spectra is what one would expect from the behaviour of mercury in the visible and ultra-violet, for the spark spectrum is rich in lines and the arc spectrum contains but few.

As has been just said, the lines at λ 1849·6 and λ 1402·5 are the two first members of the Principal Series predicted by Paschen; the third member, which should occur at λ 1268·9,

[1] Loc. cit. [2] Loc. cit.
[3] "Trans. Roy. Soc. Canada," 20, p. 377, 1926.
[4] "Proc. Roy. Soc.," 112, p. 95, 1926.
[5] "Trans. Roy. Soc. Canada," 19, p. 89, 1925.
[6] "Astrophysical J.," 38, p. 282, 1913.
[7] "Ann. d. Phy.," 42, p. 825, 1913.
[8] "Comptes Rendus," 155, p. 141, 1912.

is within the limit of the transparency of fluorite, but was not found. This was to be expected, for, as the intensity falls off very rapidly between λ 1849·6 and λ 1402·5, the next line in the series must be very faint indeed. The member of the Combination Series found by Wolff at λ 1435·6 was not observed with the grating.

Hughes [1] predicted the nature of the spectrum of the mercury arc in the Schumann region, basing his conclusions on photo-electric data. Later experiments [2] have somewhat changed his numerical values. Neither the original prediction nor the corrected data agree accurately with the spectrum as actually observed.

The observations which have just been discussed were obtained after the spectroscope had been repeatedly exhausted and washed with dry hydrogen. If a photograph was taken with air in the spectroscope, the appearance of the line at λ 1849·6 was profoundly modified. The broad line, which often extended over thirty Ångströms, was now replaced by three groups of rather faint, sharp lines. This is, undoubtedly, the phenomenon observed by Steubing,[3] and this is the phenomenon which all investigators will observe who work with an apparatus in which the light from the mercury arc must traverse a considerable air-path before falling on the photographic plate. It is possible that some of Tian's [4] measurements refer to the strongest of these lines or bands. Except for these lines, there is nothing visible in the mercury arc below λ 1900 when investigated through air.

Steubing has attributed the lines to the fluorescence of oxygen, and their narrowness and sharpness lend colour to this interpretation. It is almost certain, however, that the effect is produced by the absorption of the air after the light has passed through the slit of the spectroscope.[5] The lines in question belong to the tenth band, as observed by Leifson [6]

[1] "Phil. Mag.," 21, p. 393, 1911.
[2] "Phil. Trans. Roy. Soc. Lond.," 212, p. 205, 1912.
[3] "Ann. d. Phy.," 33, p. 572, 1910.
[4] "Comptes Rendus," 152, p. 1483, 1911.
[5] L. and E. Bloch, "Comptes Rendus," 158, p. 1161, 1914.
[6] "Astrophysical J.," 63, p. 78, 1926.

in oxygen. The strong and broad mercury band at λ 1849·6 forms an excellent background for the detection of such radiations.

When the mercury arc in quartz is employed in photo-chemical, biochemical, and photo-electric experiments, it is obvious that very different results may be expected if the light has to traverse a short air-path from those which will result if the air-path is long. In the first case, the full energy of the great line at λ 1849·6 will be effective; in the second, only the feeble action of Steubing's lines will be felt. It is well for workers in these fields to bear this fact in mind. Experiments show that biochemical, like photo-electric action, increases with decrease in wave-length. It is, therefore, this line λ 1849·6 which, of all lines in the mercury spectrum, is the most active in producing *abiotic* effects when the organisms under observation can be brought into close proximity to the lamp. In this connexion, one must remember that even fused quartz is often sufficiently transparent to transmit this radiation strongly. On the other hand, it must not be forgotten that water in thickness of even 1 mm. is very opaque at λ 1850.[1] The scarcity and feeble nature of the other lines in the Schumann region renders the mercury arc inefficient in producing effects which depend on shorter wave-lengths. For example, the light from the mercury arc produces far less volume ionization than results from the use of a hydrogen tube.

With a lamp made entirely of quartz, the line λ 1774·9 is the most refrangible radiation on the plate. The fact that the spectrum terminates at this point is probably due to two causes: first, the absorption of the quartz; and second, the absorption of the dense mercury vapour itself. The broad line or band at λ 1849·6 is always unsymmetrical, the maximum of intensity lying well toward the more refrangible side. With the quartz lamp, the band is always strongly reversed; the width of the whole band is usually about 30 or 40 units; the reversed portion is about 6 units wide.

When the lamp with the fluorite window was employed,

[1] Lyman, "Nature," 84, p. 71, 1910.

it was constantly kept in connexion with a vacuum pump; even then, the line at λ 1849·6 was sometimes reversed. It was also very sensitive to the presence of films on the window. This may partly explain the decay of the efficiency of the mercury arc with time, which has been recorded by several observers. In the quartz arc, however, where the whole system remains very hot, the formation of films is probably not the important factor. The observed effect may well be due, in part, to a change in the quartz itself under the action of the ultra-violet light, similar to that which has been observed with fluorite. With this substance, long exposure in the Schumann region will turn transparent, colourless fluorite into an opaque modification of a purple tinge. Dr. Nutting has observed the same change of colour with glass.

It is interesting to note that Steubing's lines were obtained both with the quartz lamp and with the arc at low pressures.

The first work on the spark spectrum was done with the vacuum grating spectroscope at Harvard.[1]

The arrangement for studying the spectrum was exactly similar to that employed in the work on the spectra of the alkali earths. A strontium amalgam, a barium amalgam, and a globule of mercury were used successively as terminals. The spark was in an atmosphere of hydrogen. The spectra are characterized by numerous lines extending from λ 1876 to the limit set by the transparency of fluorite. All the strong lines lie between λ 1876 and λ 1650.

The strontium amalgam contained 75 per cent of mercury. The barium amalgam contained 80 per cent of mercury. When pure mercury itself was employed, it was held in a steel cup; the upper electrode was a point of soft steel. The three spectra obtained in this way are nearly identical. The spectrum from pure mercury, however, is quite feeble on the more refrangible side—in fact, beyond λ 1750 all the lines are very faint, and the group beyond λ 1350 cannot be seen at all. This is probably due to the absorption of the metallic vapour round the spark. That the lines between

[1] Lyman, "Astrophysical J.," 38, p. 282, 1913.

λ 1750 and λ 1260 are due to mercury itself is proved by the behaviour of the amalgams. For, though the strontium amalgam was of rather doubtful character, the barium amalgam was known to be pure. The spectra of these two substances were identical; it seems probable, therefore, that their common spectrum is due to their common ingredient, namely, mercury.

The line λ 1849·6, so strong in the arc, appears in the amalgam spectrum as a faint band; it is reversed in the spark from mercury itself. Of the remaining six arc lines, only two surely appear in the spark.

Work on the mercury spectrum from a vacuum tube in the region below λ 1900 was carried on only at pressures under 3 or 4 mm. and has been mostly incidental to the study of gas spectra. Only one line has been recognized, that at λ 1849·6.

The spectrum of the vacuum spark has been measured recently by Carroll [1] between λ 740 and λ 1750. L. and E. Bloch [2] give wave-lengths for the spark in hydrogen between λ 1414 and λ 1641. The ultra-violet on the less refrangible side of λ 1880 has been covered by Bayen [3] and by Déjardin.[4]

Thallium.—The most satisfactory measurements of the vacuum spark spectrum are those of Carroll,[5] covering the range λ 993 to λ 4200. This investigator recommends the lines of this element as standards because of their number, and because of the accuracy which has been attained in their measurement. The spectrum of the spark in nitrogen at atmospheric pressure is given by L. and E. Bloch.[6] McLennan, Ainslie, and Fuller [7] give lines in the arc spectrum between λ 1478 and λ 1907.

Lead.—The spectrum of the vacuum spark has been measured by Carroll [8] between λ 767 and λ 1936. Lang [9] gives wave-lengths to λ 408. For the spectrum of the spark

[1] "Trans. Roy. Soc. Lond.," 225, p. 357, 1925.
[2] "Journ. de Phy.," 2, p. 229, 1921.
[3] "Comptes Rendus," 180, p. 57, 1925.
[4] *Ibid.*, 183, p. 1340, 1926.
[5] Loc. cit.
[6] "Comptes Rendus," 178, p. 472, 1924.
[7] "Proc. Roy. Soc.," 95, p. 318, 1919.
[8] Loc. cit.
[9] "Trans. Roy. Soc. Lond.," 224, p. 371, 1924.

in nitrogen see L. and E. Bloch.[1] The vacuum arc spectrum has been measured by McLennan, Ainslie, and Fuller [2] between λ 1431 and λ 2170. McLennan, Young, and Ireton [3] give several absorption bands between λ 1900 and λ 4058, due to lead vapour.

Bismuth.—The spectrum of the spark in nitrogen has been measured by L. and E. Bloch.[4] Wave-lengths from λ 670 to λ 2022 for the vacuum spark are given by Lang.[5] The spectrum for the arc in vacuum has been investigated by McLennan, Young, and Ireton.[6]

Uranium.—Lang [7] has measured the spectrum of the vacuum spark between λ 397 and λ 2008.

Very little work has been done on the emission spectra of gaseous compounds in the extreme ultra-violet. The facts which are given in the following paragraphs are for the most part not new, but they possess a certain historical and practical value.

Oxides of Carbon.—In the extreme ultra-violet the spectra of two gases are readily obtained; the one is due to hydrogen, the other to a compound of carbon. This latter spectrum consists of a great number of bands; it appears to begin in the ultra-violet near λ 2100 and extends to the neighbourhood of λ 1300. It was early recognized by Schumann. It has also been studied with the grating spectroscope; [8] the resulting wave-length measurements are given in Table VII. These data are valuable since they afford points of reference in the region between λ 1854 and λ 1675, where few lines exist.

The appearance of the spectrum is shown in Plate VIII, Vol. 13, of the "Memoirs of the American Academy." It is marked "Air," because the carbon compound which gives rise to it is usually found in discharge tubes which have been exhausted for the first time. The bands are most intense in the less refrangible region, but they are all of the same general

[1] Loc. cit. [2] "Proc. Roy. Soc.," 95, p. 316, 1919.
[3] "Trans. Roy. Soc. Canada," 13, p. 7, 1919.
[4] Loc. cit. [5] Loc. cit.
[6] "Proc. Roy. Soc.," 98, p. 95, 1920. [7] Loc. cit.
[8] Lyman, "Proc. Am. Acad.," 45, p. 315, 1910.

type, with heads directed toward the region of shorter wave-length. The strongest bands are evidently double. The system, at least throughout its less refrangible part, forms a continuation of the "Fourth Group," as described by Deslandres in his paper, "Spectre de bandes ultra-violet des composés hydrogenés et oxygénés du carbone." [1] The spectrum under investigation is thus related to the series of bright bands in the visible and the ultra-violet attributed to carbon monoxide and often observed in ill-prepared vacuum tubes.

It is only too easy to obtain the bands in the region of short wave-lengths, for, to quote Schumann himself,[2] they are "the unwelcome attendants of all my spectra." In order to determine the cause of the phenomenon, however, experiments were made with both carbon monoxide and carbon dioxide and with a variety of conditions in the discharge tube. The results of these experiments may be stated as follows: Exactly the same bands are obtained when carbon monoxide is used as when carbon dioxide is employed, but in the former case the strength of the whole spectrum is considerably greater than in the latter. With increased current strength from a transformer, between five and twenty milliamperes, the intensity of the bands increases in a uniform manner throughout the extent of the spectrum. When a spark gap is placed in series with the tube, and a condenser is introduced in such a way as to produce a disruptive discharge, the spectrum at first weakens and then vanishes altogether.

The effect is accomplished by a very marked decrease in pressure in the tube and by the formation of a dark deposit on the walls of the capillary. These experiments go to confirm the results of Schumann, as they show that the spectrum is due to carbon monoxide. The occurrence of the bands when carbon dioxide is present may be explained by the fact that this gas is known to be transformed into carbon monoxide under the influence of light and the electric discharge.[3] The disappearance of the spectrum with the disruptive discharge

[1] "Comptes Rendus," 106, p. 842, 1888. [2] Loc. cit., p. 16.
[3] Hirchefinkel, "Comptes Rendus," 149, p. 395, 1909.

is due to the destruction of the carbon monoxide. The oxygen set free by the reaction seems to combine with the electrodes, while the carbon is deposited. This property of a condenser discharge is useful, since it permits the spectroscopist to free his apparatus of an annoying impurity. The decrease in pressure which accompanies this reaction is often a striking and important phenomenon.

In addition to their value as standards of wave-lengths, the results are of some theoretical importance. Deslandres in the paper just quoted has used his measurements of the carbon spectrum to test his "Rules." As the spectrum under discussion seems to form a continuation of that described by Deslandres, it is interesting to see if its bands also show the numerical relations described by the earlier investigator. In making the comparison, however, it is necessary to confine the attention to those relations which deal with the heads of the bands, for the dispersion employed did not permit of the study of the lines of which each band is composed. It must also be remembered that the region of high frequencies is not perfectly adapted to such a test, since a small error in the wave-length is magnified in relations which deal with frequencies.

The laws under discussion are two in number: first, that a group of bands may be broken up into sets of series such that the differences in frequency of the heads of the bands in any one series form an arithmetical progression; second, that all the series are similarly constructed. The first rule may obviously be stated in another way—the second differences of the frequencies of the heads of the bands in any one series are constant.

Deslandres has analysed his "Fourth Group" into five series, characterized by small and not very regular second differences. With the aid of the measurements in the extreme ultra-violet, it has been found possible to follow the arrangement into the region between λ 2000 and λ 1600 and to add seven new series of the same type.

On the more refrangible side of λ 1600, however, matters are not very satisfactory. The bands must be arranged into series showing very large second differences which are only

approximately constant. These series might be considered as constituting a " Fifth Group."

The spectrum contains a great many bands which are either too feeble to measure or whose positions are made uncertain by the tails of stronger bands; if these could be included in the series, a better system would probably result.

So much, then, for the earlier attempts to analyse the spectrum of carbon monoxide. The modern theory of band spectra in the hands of Birge [1] has clarified the whole subject, and has shown the relation of the bands in the extreme ultra-violet to the rest of the radiations from the gas in question. More recently Hopfield and Birge [2] have published additional data on the bands from this oxide of carbon.

[1] " Phy. Rev.," 28, p. 1157, 1926. [2] *Ibid.*, 29, p. 922, 1927.

CHAPTER IV.

PHOTO-ELECTRIC PHENOMENA. THE EXTENSION OF THE SPECTRUM.

The preceding pages have given some account of the properties of light of very short wave-length from the point of view of the student of spectroscopy. The scope of the work does not permit of a detailed treatment of photo-chemical, photo-electrical, and photo-abiotic phenomena, but, as they attain very striking proportions in the Schumann region, a brief description of some simple experiments which show their variation with the wave-lengths of the exciting light is here included.

Attention has already been called to the rapid increase in ozone-producing power as one proceeds into the region on the more refrangible side of λ 1850. Much the same thing is observed in photo-electric action, though to an even greater degree.[1] In the case of volume ionization the effect is so striking and so easily shown to an audience that the apparatus itself merits description. A discharge tube like that illustrated on page 76 is closed by the usual fluorite window; directly above this is arranged a separate chamber or screen cell about 1 cm. thick which is, in turn, closed with fluorite. The discharge tube must be filled with hydrogen to a pressure of 2 or 3 mm. A gold-leaf electroscope of any simple type has for its terminal electrode a strip of metal about 1 cm. wide by 3 cm. long, which, protruding from the metallic case, is protected by a gauze cylinder. This strip is placed within 5 or 6 cm. of a window of the screen cell just mentioned, a blast being arranged to sweep the window and to carry the air from its neighbourhood through a hole in the gauze

[1] Lyman, "British Association Report," p. 134, 1909.

cylinder against the strip. If now the screen cell is full of air and the blast turned on, no effect is produced in the leaves of the electroscope when the discharge tube is excited; but if the cell is exhausted, the leaves of the spectroscope collapse quite rapidly. The cell when filled cuts off the Schumann rays; but when it is exhausted it allows the rays to pass and they produce volume ionization in the surrounding gas. The fact that a thickness of about 1 cm. of air is sufficient to stop the action entirely, shows that the active rays belong in the region on the refrangible side of λ 1850. The experiment is a crude adaptation of the more complex procedure employed by Palmer.[1]

Turning to the bactericidal properties of light, the action has long been known to increase with decrease in wave-length and a great mass of information has been accumulated relating to the less refrangible side of λ 2000, the use of a quartz mercury lamp for the sterilization of water being a good illustration of an application of this knowledge to a practical problem. A rather simple experiment may be performed to illustrate the fact that the action continues to increase in a striking manner after the Schumann region is entered. A discharge tube filled with hydrogen and closed at one end with fluorite is placed under the stand of a microscope in such a way that the field of vision may be illuminated by a beam of light from a small arc lamp arranged to pass directly through the tube. Some mobile form of organism, such as the infusorian-like Colpoda or the swarmspore-like Spherella, is placed in a drop of water on this fluorite window; the motions of the organisms may then be watched through the microscope. If now, while one of these bodies is the field of view, the discharge tube be excited by an alternating current of, say, 10 milliamperes, the power of motion is almost immediately lost. In many cases an exposure of two or three seconds is sufficient to produce the result. With Colpoda, not only does motion cease, but the whole body breaks down and becomes miscible with the water. This destruction of cell structure is by no means confined to the organisms just mentioned; it may be

[1] "Phy. Rev.," 32, p. 1, 1911.

seen in a great variety of tissue. It is necessary only that the specimen should be penetrable by the active rays. The experiment may be modified by interposing a screen cell of air of the kind already described or by the use of a thin plate of rock-salt between the source of the Schumann rays and the specimen. In this way it is easily shown that the active rays lie for the most part on the more refrangible side of λ 1750. By the use of a micro-projection in connexion with a discharge tube of special form, it is quite possible for a number of persons to see the phenomena at the same time.

The strong abiotic action of the hydrogen spectrum in the extreme ultra-violet has an interesting bearing on the hypothesis which maintains that living organisms may be transported through interplanetary space. For it is obvious that if light of the proper wave-length escape from the sun, the space in question would be effectively and continually sterilized. The lack of atmosphere and of heat is no bar to the action, for it has been shown that oxygen and moisture are not necessary to this bactericidal phenomenon, and that abiotic action continues at the temperature of liquid air. It might be contended that the gases which surround the sun effectively prevent the escape of Schumann rays; but if sun spots are accompanied by jets of burning hydrogen projected through the solar envelope, this objection falls to the ground. The burning hydrogen would provide the necessary abiotic rays. In short, it seems probable that interplanetary space is a germ-free space.

Apart from points of general interest connected with photo-chemical, photo-electric, and photo-abiotic effects, the extreme ultra-violet offers a field for measurements of theoretical importance. Einstein's equation $\frac{mv^2}{2} = h\nu - k$, which connects the velocity of photo-electrons with the frequency of the light by which they are liberated, has been tested for radiations on the less refrangible side of λ 1850 and in the region of the X-rays.

Sabine [1] has carried the investigation into the Schumann

[1] "Phy. Rev.," 9, p. 210, 1917.

region; his results are in general agreement with the equation. Further investigations of photo-electric phenomena in the extreme ultra-violet are likely to yield facts of importance.

Returning to the rapid increase in various photo-activities with the change in the nature of the light, the matter will be clearer if the period is taken as the fundamental parameter rather than the wave-length, a proceeding which is amply justified by theoretical considerations. A scale plotted on this system serves to emphasise the obvious fact that for a given decrement in wave-length the corresponding increment in frequency is far greater on the border of the Schumann region than on the corresponding border of the ultra-violet. An extension of the spectrum by a definite number of wave-lengths in the Schumann region is, therefore, more productive of important consequences than an equal extension in the ultra-violet, if these consequences are measured by phenomena whose magnitude depends on the frequency of light.

The Extension of the Spectrum.

Early experiments which attempted to show an extension of the spectrum by indirect means were few in number and not perfectly conclusive. Wood [1] has observed that the spark produces a radiant emission which gives rise to luminescence in the nitrogen of the air. Fluorite 1 mm. thick cuts off the emission, but a very thin piece permits the emission to pass to a slight degree; this might lead to the conclusion that the effect is due to light which lies on the more refrangible side of the fluorite absorption band.

Lenard [2] has reported the existence of an emission from an aluminium spark which he detected by its ionizing action. It penetrated 4 cm. of air and both quartz and fluorite. An experiment with a fluorite lens led him to ascribe to these rays a refractive index which would ordinarily belong to light between λ 1400 and λ 1370. That the rays were not of this

[1] "Phil. Mag.," 20, p. 707, 1910; *ibid.*, 27, p. 899, 1914.
[2] "Sitz. Heidelberg Akad. d. Wiss. Abhand.," p. 31, 1910.

wave-length is shown by their transmission through quartz, which is known to be opaque to this part of the spectrum. Lenard explains the index obtained, by ascribing the emission to the more refrangible side of the absorption fluorite. The discovery of the relative transparency of air in the neighbourhood of λ 1150 [1] lends some colour to this hypothesis, though the more refrangible limit of the absorption of the quartz and fluorite has not been discovered by spectroscopic means.

In conclusion, it is necessary to describe the work by which the spectrum has been extended in the last dozen years, and to discuss the attempts which have been made to bridge the gap between optical spectra and the region of soft X-rays.

We have seen that the Schumann region was extended by removing absorbing material from the light paths—a process which involved the use of a concave diffraction grating ruled on speculum. At the time when the first edition of this book was published, the limit of the spectrum was in the neighbourhood of λ 900. Without altering the general arrangement of the apparatus, but by improvements in technique, such as the employment of better vacuum pumps, and especially by the use of a more powerful source, the author succeeded, in 1915,[2] in extending the spectrum to λ 600. Two years later he pushed the limit to λ 500.[3] The results which attended the efforts of Millikan [4] were due almost entirely to the fact that he successfully employed a new source, the vacuum or hot spark. This type of discharge, first described by Wood,[5] is particularly rich in radiations of the shortest wave-lengths. The present limit of the optical spectrum near λ 140 was set by Millikan.

In reply to the question as to what are the causes which confine the spectrum to its present limit, it may be said that the nature of the source and the reflecting power of the grating

[1] Hopfield, " Phy. Rev.," 20, p. 587, 1922.

[2] " Proc. Nat. Acad. Sci.," 1, p. 368, 1915; " Astrophysical J.," 43, p. 89, 1916.

[3] " Science," 45, p. 187, 1917.

[4] *Ibid.*, 50, p. 138, 1919; " Astrophysical J.," 52, p. 47, 1920; " Proc. Nat. Acad. Sci.," 7, p. 289, 1921.

[5] " Phy. Rev.," 5, p. 1, 1897.

are the two chief factors. The sensitivity of the Schumann plate, though of great importance, is probably not responsible for the limit of the spectrum.

With respect to the first factor, it is true that the intensity of the lines of the shortest wave-length depends on the energy supplied to the source; thus, with increasing energy of excitation the spectrum may appear to extend. Even a quartz discharge tube will give radiations of nearly as short wave-length as the vacuum spark, if excited with sufficient violence; there is, however, a limit beyond which it is practically impossible to go in this direction. On the other hand, it may be that all available sources are weak in radiations lying in the region under discussion, that is, between λ 20 and λ 150, even though, like the vacuum spark, they produce rather penetrating X-rays quite strongly. It is interesting to note in this connexion that Hoag [1] has been unable to push the spectrum of the vacuum spark beyond λ 200, though he employed a concave grating on speculum at grazing incidence, an arrangement which one might expect to be very favourable for the detection of faint radiations.

At this point it may be well to mention that the writer has attempted to obtain the characteristic radiation from magnesium at λ 320·9 and λ 323·2, and from carbon at λ 45, by bombardment from a Coolidge cathode, the target being of the material under examination. In the case of magnesium the applied potential was 5300 volts, the current 10 milliamperes, and the time of exposure twenty-four hours. With carbon the voltage was 9700 volts, current 10 milliamperes, time of exposure thirty-one hours; the results were entirely negative.

The fact that both Millikan and the author have obtained the lines in magnesium with a vacuum spark shows that the lack of success in the case of this metal was not due to the reflecting power of the grating, but to the character of the source.

In considering the part played by the reflecting power of the grating, it will be well for the moment to confine our attention to the case of normal incidence, for it was under

[1] "Astrophysical J.," 66, p. 225, 1927.

this condition that the work of Millikan was carried on. The question may be divided into two parts: first, the effect of surface layers; and second, the intrinsic reflecting power of the substance under examination. That layers of oxide or of grease have a very strong tendency to thrust the limit of the spectrum toward longer wave-lengths, there can be no doubt whatever. How far gases clinging to the grating surface are involved is unknown; experiments along this line might be of interest. That the material of which the grating is made is all-important goes without saying. The author has shown that glass is superior to speculum on the short wave-length side of λ 500, but that quartz is hardly better than glass.

On the other hand, Millikan's work, which resulted in establishing the present limit, was done with a series of gratings freshly ruled on speculum. Under very exceptional circumstances, therefore, a grating on speculum may produce a spectrum extending farther into the extreme ultra-violet than that obtained from an instrument ruled on glass or quartz. This emphasises the fact that the part played by surface layers is most important, and cannot be easily disentangled from the intrinsic reflecting power of the material of which the grating is composed.

We may now turn to the attempts which have been made to bridge the gap in the spectrum from the side of soft X-rays. As we have seen, this gap is very narrow, if measured in terms of wave-length; it may be said to extend from the limit of X-rays reached by Thoraeus [1] at λ 21, to the shortest wave-lengths in optical spectra obtained by Millikan near λ 140.

The method of critical potential, as employed by Richardson [2] and many others, offers an indirect means of attacking the problem, and by it the gap may be said to have been crossed some years ago. But investigations of this type involve so many difficulties and uncertainties that the results obtained by them cannot be regarded as entirely conclusive. Investigations based on the use of those principles of interference and diffraction which have been tested in the region

[1] "Phil. Mag.," 1, p. 312, 1926.
[2] "Proc. Roy. Soc.," 110, p. 247, 1926.

of optical spectra and in the domain of the X-rays appear to be far more promising.

The crystal lattice and the ruled diffraction grating are the two instruments which have been employed.

Dauvillier [1] has followed a technique similar in general theory to that used in the study of X-rays: he secured the large grating-space necessary for work in the region under discussion by employing a crystal of a fatty acid. The source consisted of a target coated with the material under examination, bombarded by electrons from a hot cathode. With several substances it was found essential to work with a thin, freshly deposited surface on the target; this surface was secured in the case of thorium by making the filament itself of the substance under investigation, the spatter from this filament then provided the necessary coating. Currents of the order of 25 milliamperes at 2800 volts were used; to prevent fogging the photographic plate, the source was separated from the body of the spectroscope by a thin window of magnesium. An excellent vacuum was obtained in the whole apparatus. Among the radiations obtained by Dauvillier are carbon K_α at λ 45·5, and boron K_α at λ 73·5. He also gives a number of lines due to thorium; they occur at λ 45·3 (identical with carbon), λ 48·2, λ 51·5, λ 71·0, and λ 121. This last line represents the longest wave-lengths obtained by the use of a crystal lattice.

The results have been criticized by Thoraeus [2] on the ground that magnesium, of which the window used by Dauvillier was made, is known to be opaque for radiations of wave-lengths longer than λ 10 or λ 15.

A. H. Compton,[3] by employing a plane diffraction grating ruled on speculum, has succeeded in measuring the wave-length of the K_α line of molybdenum at λ 0·7. It is essential that the grating should be used at grazing incidence, for the method depends for its success upon the fact that the radiation is totally internally reflected at the grating surface, the

[1] "Journal d. Phy.," 8, p. 1, 1927.
[2] "Nature," 27 Nov., p. 771, 1926.
[3] "Proc. Nat. Acad. Sci.," 11, p. 598, 1925.

material of the grating playing the part of the rarer medium with respect to the vacuum which surrounds it. Something has already been said [1] on the technique involved in the use of a grating in this manner.

Thibaud [2] has repeated Compton's experiments with X-rays, and has carried his investigations into the region of longer wave-lengths. He employed two plane glass gratings at grazing incidence, one of 200, the other of 1180 lines to the millimetre. A target bombarded by electrons from a hot cathode served as source; no window separated this source from the body of the vacuum spectroscope. He records [3] a number of wave-lengths, among which are the following:

$K_aO = \lambda\ 23{\cdot}8$; $K_aN = \lambda\ 31{\cdot}8$; $K_aC = \lambda\ 44{\cdot}9$; $K_aB = \lambda\ 68$.

The K_a radiation from boron at λ 68 is the longest wave-length which he has obtained.

He explains the difference between his values and those of Dauvillier for carbon and for boron on the ground that Dauvillier made no allowance for the refraction of the radiation into the crystal which he employed.

Hunt,[4] independently of Thibaud, but using essentially the same method, has measured the K_a line from carbon.

It is interesting to note in passing that both Thibaud and Hunt used an ordinary photographic plate. Apparently the chief advantage of employing Schumann plates for work with soft X-rays arises from the fact that they are not easily fogged by visible light.

Osgood, working in Compton's laboratory,[5] has employed a concave glass grating of 215 cm. radius and 800 lines per millimetre, at grazing incidence. By means of bombardment from a low temperature, oxide-coated filament, he has obtained radiations extending from the K_a line of carbon near λ 45 to a line which he ascribes to iron at λ 215. The disintegration of the coating of the filament, with the consequent

[1] See p. 58.
[2] "Journal d. Phy.," 8, p. 13; and p. 447, 1927.
[3] "Comptes Rendus," 185, p. 642, 1927.
[4] "Phy. Rev.," 29, p. 919, 1927.
[5] *Ibid.*, 30, p. 567, 1927.

deposit of a layer of uncertain composition on the target, rendered the interpretation of the spectrum obtained somewhat difficult. In view of the great importance of the results, it is most desirable that these experiments should be confirmed and extended.

To sum up: Millikan, working with a concave grating at normal incidence, has advanced from the side of the extreme ultra-violet to the neighbourhood of λ 140. Dauvillier, coming from the region of the X-rays, and by use of a crystal lattice, has reached λ 121. Thibaud, with a plane grating at grazing incidence, records λ 68 as his longest wave-length. Finally, the work of Osgood serves to fill completely the gap in the spectrum.

INTRODUCTION TO TABLES.

The author's early measurements of the spectra of hydrogen and carbon monoxide are reprinted, with the hope that they may serve as convenient points of reference in the Schumann region. For a more extended list of the lines in the hydrogen spectrum, the reader should consult Hori.[1]

The measurements of the spectra of carbon, nitrogen, oxygen, and aluminium are collected from various sources. The list of lines is not complete in all cases, but it is to be hoped that the identifications are correct.

The values of the intensities are by no means satisfactory. For any one observer, the numbers given in the table present a fair idea of the relative strength of the lines; but in going from the data of one observer to those of another, this may not be the case. This state of affairs arises, not only from differences in judgment, but also from differences in the character of excitation. In particular, the values in aluminium marked P were obtained by Sawyer and Paschen with a hollow cathode, a condition very different from the hot spark which served as source for a majority of the other radiations recorded under the element. The scale of the intensities given by Sawyer and Paschen, then, has no simple relation to the other scales in this particular table.

[1] "Zeitsch. f. Phy.," 44, p. 834, 1927.

TABLES.

WAVE-LENGTHS IN VACUUM.

TABLE I.—SPECTRUM OF HYDROGEN.

Wave-Length.	Intensity.	Character.	Wave-Length.	Intensity.	Character.
1228·3	8		1279·8	5	
1230·1	8		1281·2	4	
1231·0	1		1282·6	1	
1232·1	5		1283·4	6	
1234·3	4		1284·5	5	double
1235·8	6		1286·9	5	double
1239·6	3		1288·1	4	
1241·5	2		1289·4	3	
1246·1	4		1290·4	5	
1247·2	4		1291·3	2	
1248·0	2		1293·6	6	double
1249·8	3		1295·7	2	double
1251·2	3		1297·4	5	
1253·2	6		1299·5	1	
1253·9	5		1300·0	3	double
1255·5	4		1302·5	2	double
1257·1	4		1307·5	2	
1258·2	4		1311·1	2	
1259·9	4		1312·9	2	
1261·9	8		1314·7	1	
1264·0	1		1315·6	1	double
1264·6	5		1319·2	4	
1265·8	4		1323·4	5	
1267·3	1		1325·0	5	double
1268·3	1		1327·1	3	
1269·1	3		1327·5	2	
1269·9	1		1329·3	1	
1270·7	4		1331·3	6	
1271·5	4		1333·9	8	double
1272·0	1		1335·3	2	
1273·3	3		1336·1	8	double
1274·2	1		1337·6	6	
1275·0	3		1338·7	7	double
1276·1	1		1340·9	1	double
1277·1	6	double	1342·4	8	
1279·0	1		1343·6	1	

TABLE I.—SPECTRUM OF HYDROGEN (*continued*).

Wave-Length.	Intensity.	Character.	Wave-Length.	Intensity.	Character.
1345·4	8	double	1411·8	1	
1347·2	9	double	1413·0	8	
1349·1	2		1414·9	2	
1350·2	3		1416·4	3	
1350·8	3		1419·5	2	
1352·5	8		1420·3	3	
1353·6	8		1426·8	3	
1355·5	7		1427·8	7	double
1357·3	6		1429·0	3	
1358·2	4		1430·1	7	
1359·2	5		1431·1	3	
1360·1	5		1433·0	8	double
1362·4	1		1434·3	3	
1363·4	8		1435·2	4	
1364·3	3		1436·3	7	double
1365·8	5		1438·0	4	
1366·5	1		1439·1	1	
1367·6	3	double	1441·0	8	
1368·0	3		1442·8	1	
1369·1	1	double	1443·6	7	
1370·4	2		1445·2	4	
1371·3	6		1446·2	6	
1372·1	1		1447·4	2	?
1372·9	3		1449·2	2	
1374·0	1		1450·3	5	
1374·5	2		1451·0	1	
1375·5	1		1452·0	3	
1376·1	1		1452·5	1	
1377·2	6	double	1454·3	1	
1378·0	1	double	1455·1	7	double
1380·2	5		1456·3	4	
1380·8	1		1457·4	6	
1382·9	1		1458·4	6	
1383·0	1		1460·1	5	double
1384·2	1		1461·0	4	
1385·6	2		1462·0	3	
1386·3	3		1462·9	4	
1387·7	4		1463·9	8	
1390·0	1	double	1465·2	3	
1391·2	1		1467·2	6	double
1393·2	3		1468·6	6	
1394·0	7	double	1471·0	3	
1395·2	2		1472·5	3	
1396·4	7		1473·9	5	
1397·5	6		1474·9	4	
1398·0	1		1476·4	4	
1399·0	7		1477·3	3	
1400·6	1		1478·9	2	
1402·0	4		1479·7	4	
1402·8	8		1480·4	4	
1404·3	5		1481·7	5	
1405·5	2		1482·1	1	
1407·3	7		1483·7	3	
1408·6	3		1486·1	1	
1410·5	8	triple	1486·9	9	

TABLE I.—SPECTRUM OF HYDROGEN (*continued*).

Wave-Length.	Intensity.	Character.	Wave-Length.	Intensity.	Character.
1487·8	1		1563·0	1	
1489·3	6		1564·0	1	
1489·9	3		1565·1	3	double
1491·9	7		1567·1	5	double
1492·7	1		1569·2	6	
1494·1	3		1569·7	1	
1495·5	10	double	1571·3	1	
1499·8	8		1571·7	7	
1502·2	2		1574·3	5	
1503·9	1		1577·2	8	
1505·0	8		1579·2	4	
1505·9	1		1581·0	7	double
1506·6	1		1584·1	7	
1511·5	8		1585·7	7	double
1513·6	7		1587·6	3	
1515·0	6		1589·0	8	triple
1516·4	5		1590·9	4	
1517·5	6	double	1591·5	8	
1519·0	6		1593·6	7	
1520·1	5		1595·2	1	
1521·7	2		1596·2	10	
1522·5	2		1599·4	6	
1523·4	8		1602·0	8	
1525·4	5		1602·8	1	
1526·6	2		1603·8	1	
1527·5	4		1604·6	6	
1529·7	3		1605·3	5	
1530·9	6		1606·3	5	
1532·1	6		1607·7	10	
1533·2	6		1608·2	6	
1535·0	6	double	1608·6	10	
1536·7	1		1609·2	3	
1537·5	7	double	1610·1	2	triple
1539·2	5		1610·5	7	
1539·9	2		1611·2	1	
1540·6	2		1611·8	3	
1541·6	7		1612·5	1	
1543·9	2		1613·3	7	
1544·7	8		1614·3	4	
1545·5	2	double	1615·0	3	
1546·4	6		1616·7	6	
1547·4	7	double	1617·9	1	
1548·3	1		1619·9	2	double
1549·9	7	double	1621·1	7	double
1550·6	7	double	1622·1	3	
1551·5	2		1623·2	2	
1553·3	10		1623·8	7	
1554·9	3		1625·8	4	
1555·6	1		1627·6	1	
1556·4	2		1628·5	8	
1557·4	1		1631·7	2	
1558·7	1		1633·7	6	
1560·0	1		1634·1	4	
1561·1	2		1635·3	3	
1562·2	4		1636·5	7	

TABLE I.—SPECTRUM OF HYDROGEN (*continued*).

Wave-Length.	Intensity.	Character.	Wave-Length.	Intensity.	Character.
1638·2	4		1647·8	1	
1639·1	5		1651·8	1	
1639·7	1		1654·2	2	
1640·5	6		1662·9	1	
1641·6	5		1667·4	2	
1643·0	5		1670·2	1	
1644·6	7		1671·6	2	
1645·7	2		1672·4	2	
1646·0	1		1674·6	1	

TABLE II.—HELIUM.

Principal OS — *m*P. OS = 198,298.				
I.	λ obs.	λ calc.	ν.	*m*
10	584·40		171,115	1
7	537·12	537·08	186,178	2
5	522·21	522·26	191,493	3
4	515·65	515·67	193,930	4
3	512·09	512·15	195,278	5
2	510·05	510·05	196,059	6
1	508·59	508·69	196,622	7

OS — 1 π.		
3	591·56	591·45

OS — 1 S (?).		
6	600·3 ± ·6	601·44

HELIUM.

$\nu = 4N\left(\frac{1}{2^2} - \frac{1}{m^2}\right)$.				$\nu = 4N\left(1 - \frac{1}{m^2}\right)$.			
I.	λ obs.	λ calc.	*m*.	I.	λ obs.	λ calc.	*m*.
5	1640·4	1640·49	3	2	303·6	303·7	2
?	1215·2	1215·18	4	1	256·3	256·25	3
?	1085·2	1084·98	5				

TABLE III.—CARBON.

M = Millikan, " Phy. Rev.," 23, p. 1, 1924.
B = Bowen, " Phy. Rev.," 29, p. 231, 1927.
B-M = " Phy. Rev.," 26, p. 316, 1925 ; and " Nature," 114, p. 380, 1924.
F = Fowler, " Proc. Roy. Soc.," 105, p. 303, 1924.
S = Simeon, " Proc. Roy. Soc.," 102, p. 489, 1923.
B-I = Bowen and Ingram, " Phy. Rev.," 28, p. 444, 1926.

I.	λ.	ν.			I.	λ.	ν.		
1	360·5	277408		M	4	945·6	105752		M
2	384·4	260166	C_{IV}	B-M	0	954·4	104775		M
4	386·4	258826		M	0	960·6	104106		M
1	419·8	238197	C_{IV}	B-M	0	966·6	103461		M
1	450·9	221769		M	10	977·031	102350·9	C_{III}	B-I
6	459·7	217552	C_{III}	B-M	5	1009·870	99022·6	C_{II}	B
1	493·7	202569		M	6	1010·09	99001·1	C_{II}	B
4	499·7	200140		M	6	1010·382	98972·5	C_{II}	B
1	511·7	195419		M	1	1022·8	97775		M
2	530·3	188590		M	6	1036·336	96493·8	C_{II}	B
1	533·9	187301	C_{II}	F	6	1037·021	96430·1	C_{II}	B
7	538·4	185742	C_{III}	B-M	8	1066·0	93812		M
1	543·4	184026	C_{II}	F	3	1092·6	91522		M
2	549·6	181953		M	3	1137·4	87920		M
2	560·5	178412	C_{II}	F	2	1141·61	87595·6	C_{II}	B
3	564·7	177086		M	4	1174·922	85112·0	C_{III}	B-I
6	574·5	174052		M	4	1175·261	85087·5	C_{III}	B-I
3	585·7	170745		M	2	1175·577	85064·6	C_{III}	B-I
2	594·79	168127	C_{II}	B	5	1175·711	85054·9	C_{III}	B-I
2	595·02	168062	C_{II}	B	4	1175·988	85034·9	C_{III}	B-I
1	598·6	167056		S	4	1176·359	85008·1	C_{III}	B-I
1	617·7	161883		M	1	1193·2	83808		S
2	636·2	157183	C_{II}	F	1	1194·4	83724		S
2	640·1	156225		S	1	1206·4	82891		S
5	641·8	155802		M	2	1209·94	82651		S
6	651·5	153483		S	2	1230·2	81289		M
1	652·1	153350		S	2	1247·391	80167·3		B-I
0	661·5	151167		M	3	1260·48	79335		S
5	687·053	145549	C_{II}	B	3	1261·2	79289		S
5	687·351	145486	C_{II}	B	4	1277·3	78290		S
1	711·0	140645		M	5	1278·7	78204		M
0	743·6	134486		M	2	1296·8	77112		M
0	749·6	133403		M	1	1310·5	76307		M
1	786·5	127141		M	2	1322·3	75626		M
5	799·9	125016		M	7	1323·79	75540		S
6	806·7	123957		M	3	1328·839	75253·7	C_{I}	B
5	810·0	123464		M	4	1329·100	75238·9	C_{I}	B
2	848·4	117876		M	4	1329·583	75211·6	C_{I}	B
5	858·088	116538	C_{II}	B	10	1334·541	74932·1	C_{II}	B-I
6	858·561	116474	C_{II}	B	10	1335·703	74866·9	C_{II} ?	B-I
1	884·8	113026		M	1	1356·2	73737		M
7	903·620	110666	C_{II}	B	5	1362·6	73391		M
8	903·960	110624	C_{II}	B	1	1426·9	70082		M
8	904·133	110603	C_{II}	B	4	1463·3	68338		S
7	904·472	110561	C_{II}	B	3	1481·7	67490		S
1	936·4	106798		M	0	1527·9	65448		M

TABLE III.—CARBON (*continued*).

I.	λ.	ν.			I.	λ.	ν.		
0	1533·1	65226		M	2	1657·37	60336·6	C_I	B
5	1548·189	64591·6	C_{IV}	B-I	2	1657·92	60316·5	C_I	B
4	1550·774	64483·9	C_{IV}	B-I	2	1658·13	60308·9	C_I	B
3	1560·257	64092·0	C_I	B-I	2	1751·8	57084		S
4	1560·660	64075·5	C_I	B-I	2	1760·44	56804	C_{II}	B
5	1561·378	64046	C_I	B-I	1	1760·85	56790·8	C_{II}	B
0	1573·5	63552		M	1	1827·3	54727		M
1	1577·6	63388		M	0	18·328	54561		M
2	1656·27	60376·6	C_I	B	5	1930·61	51797		S
3	1657·01	60349·7	C_I	B	7	1931·027	51785·9	C_{III}	B-I

TABLE IV.—NITROGEN.

H = Hopfield, " Phy. Rev.," 20, p. 582, 1922.
L = Lyman and Saunders.
K = Kayser, " Hauptlinien der Linienspektra."
B = Bowen, " Phy. Rev.," 29, p. 234, 1927.
B-M = Bowen and Millikan, " Phy. Rev.," 26, p. 154, 1925.
M = Millikan, " Phy. Rev.," 23, p. 1, 1924.
F = Fowler, " Proc. Roy. Soc Lond.," 114, p. 667, 1927.

I.	λ.	ν.			I.	λ.	ν.		
1	374·31	267158	N_{III}	B	2	772·980	129369	N_{III}	B
1	451·91	221283	N_{III}	B	2	775·9	128882		M
1	452·24	221122	N_{III}	B	1	835·71	119658		K
3	533·53	187431	N_{II}	B	6	915·603	109217	N_{II}	B
3	533·71	187368	N_{II}	B	6	915·963	109175	N_{II}	B
4	644·633	155127	N_{II}	B	6	916·018	109168	N_{II}	B
5	644·836	155078	N_{II}	B	8	916·698	109087	N_{II}	B
5	645·180	154995	N_{II}	B	2	921·978	108462	N_{IV}	B-M
0	660·3	151446		M	2	922·512	108400	N_{IV}	B-M
2	671·027	149025	N_{II}	B	1	923·037	108338	N_{IV}	B-M
3	671·397	148943	N_{II}	B	3	923·211	108317	N_{IV}	B-M
1	671·650	148887	N_{II}	B	2	923·658	108265	N_{IV}	B-M
2	671·780	148858	N_{II}	B	2	924·264	108194	N_{IV}	B-M
2	672·026	148804	N_{II}	B	7	989·803	101030	N_{III}	B
5	685·00	145985	N_{III}	B	7	991·571	100850	N_{III}	B
6	685·517	145875	N_{III}	B	1	1006·03	99400·6	N_{III}	B
6	685·822	145810	N_{III}	B	6	1083·983	92252·4	N_{II}	B
5	686·346	145699	N_{III}	B	7	1084·566	92202·8	N_{II}	B
3	746·97	133874	N_{II}	L	3	1085·540	92120·1	N_{II}	B
5	763·348	131002	N_{III}	B	8	1085·701	92106·4	N_{II}	B
5	764·358	130829	N_{III}	B	4	1101·3	90801·7	?	K
3	765·158	130692	N_{III}	B	2	1134·180	88169·4	N_{II}	F
3	771·545	129610	N_{III}	B	3	1134·421	88150·8	N_{II}	F
4	771·904	129550	N_{III}	B	3	1134·987	88106·7	N_{II}	F
4	772·384	129469	N_{III}	B	5	1158·7	86303·6	?	K
2	772·903	129382	N_{III}	B	3	1183·04	84528	N_{III}	B

TABLE IV.—NITROGEN (*continued*).

I.	λ.	ν.			I.	λ.	ν.		
3	1184·55	84420·2	N_{III}	B	0	1346·41	74271·6	N_{II}	F
0	1190·6	83991·2		M	4	1411·99	70822	N_{II}	F
3	1199·53	83365·8	N_{II}	F	6	1492·78	66988·2	N_I	L
2	1200·20	83319·4	N_{II}	F	5	1494·83	66898·5	N_I	L
1	1200·681	83286·1	N_{II}	F	1	1573·21	63564·3	N_{II}	F
3	1224·2	81686	N_{II}	F	1	1574·28	63521·1	N_{II}	F
4	1226·4	81539	N_{II}	F	2	1590·25	62883·2	N_{II}	F
4	1229·7	81321	N_{II}	F	1	1616·06	61878·9	N_{II}	F
5	1238·94	80716·7	N_V	F	1	1627·42	61447·0	N_{II}	F
4	1242·67	80472	N_I	F	1	1629·02	61386·6	N_{II}	F
5	1242·93	80457·0	N_V	F	0	1629·86	61355·0	N_{II}	F
7	1243·14	80442	N_I?	F	5	1675·83	59671·9	N_{II}	F
3	1258·75	79444	N_I?	F	5	1740·315	57460·9	N_{II}	F
1	1275·06	78427·7	N_{II}	B	7	1742·740	57380·9	N_I	B-I
1	1276·18	78359	N_{II}	B	2	1743·22	57365·1	N_{II}	F
0	1276·74	78324·5	N_{II}	B	6	1745·260	57298·1	N_I	B-I
5	1310·89	76283	N_I?	F	7	1747·855	57213	N_{II}	F
2	1319·10	75809·3	N_I?	F	10	1751·75	57085·7	N_I	F
5	1319·85	75766·2	N_I?	F	2	1763·63	56701·2	N_{II}	F
2	1326·67	75376·7	N_{II}	F	1	1765·13	56653	N_{II}	F
1	1328·01	75300·6	N_{II}	F	1	1766·08	56622·6	N_{II}	F
0	1329·43	75220·2	N_{II}	F	0	1830·71	54623·6	N_{II}	F
0	1330·80	75142·8	N_{II}	F	0	1831·78	54591·7	N_{II}	F
2	1343·37	74439·7	N_{II}	F	1	1836·36	54455·5	N_{II}	F
1	1345·29	74332·9	N_{II}	F					

TABLE V.—OXYGEN.

B = Bowen, " Phy. Rev.," 29, p. 241, 1927.
M = Millikan, " Phy. Rev.," 23, p. 1, 1924.
B-M = Bowen and Millikan, " Phy. Rev.," 27, p. 148, 1926.
H = Hopfield, " Astrophysical J.," 59, p. 118, 1924.
M-B = Millikan and Bowen, " Phy. Rev.," 24, p. 213, 1924.
F = Fowler, " Proc. Roy. Soc. Lond.," 117, p. 329, 1927.

I.	λ.	ν.			I.	λ.	ν.		
0	136·6	732332	Al?	M	1	321·5	311003		M
0	144·3	692809	Al?	M	0	328·34	304562	O_{III}	B
0	219·1	456413	Al?	M	0	335·06	298454	O_{III}	F
0	221·5	451508	Al?	M	0	345·7	289302		M
0	225·9	442693	Al?	M	0	355·06	281643	O_{III}	B
0	233·8	427807		M	0	359·4	278211		M
1	238·6	419041		M	4	374·3	267165	O_{III}	F
0	260·7	383583		M	0	379·6	263435		M
0	267·1	374420		M	2	395·52	252832	O_{III}	B
0	272·4	367121		M	2	430·06	232526	O_{II}	B
1	279·7	357513		M	2	434·91	229933	O_{III}	B
1	295·8	338043		M	0	440·49	227020	O_{II}	B
2	303·7	329294		M	1	441·93	226280	O_{II}	B
3	305·7	327129		M	0	470·30	212630	O_{II}	B

TABLE V.—OXYGEN (*continued*).

I.	λ.	ν.			I.	λ.	ν.		
2	481·53	207671	O_{II}	B	1	802·21	124656	O_{IV}	B
2	483·82	206688	O_{II}	B	8	832·754	120083	O_{II}	B
3	485·48	205982	O_{II}	B	7	832·924	120059	O_{II}	B
4	507·384	197089	O_{III}	B	9	833·327	120001	O_{II}	B
5	507·684	196973	O_{III}	B	8	833·739	119942	O_{III}	B
6	508·180	196781	O_{III}	B	10	834·459	119838	O_{II}	B
2	515·47	193998	O_{II}	B	3	835·099	119746	O_{III}	B
3	515·62	193941	O_{II}	B	9	835·288	119719	O_{III}	B
3	518·23	192965	O_{II}	B	0	898·8	111264		M
6	525·79	190190	O_{III}	B	2	921·27	108546	O_{IV}	B
3	537·813	185938	O_{II}	B	3	923·31	108306	O_{IV}	B
4	538·258	185785	O_{II}	B	1	924·92	108117	O_{I}	H
3	539·067	185506	O_{II}	B	1	925·46	108054	O_{I}	H
2	539·524	185349	O_{II}	B	1	926·33	107952	O_{I}	H
1	539·837	185241	O_{II}	B	1	926·91	107885	O_{I}	H
0	540·7	184939		M	2	929·59	107574	O_{I}	H
4	553·318	180728	O_{IV}	B	2	930·24	107499	O_{I}	H
5	554·066	180484	O_{IV}	B	2	930·87	107426	O_{I}	H
5	554·507	180340	O_{IV}	B	2	931·75	107324	O_{I}	H
4	555·270	180093	O_{IV}	B	3	936·62	106766	O_{I}	H
0	562·0	177949		M	1	938·59	106542	O_{I}	H
3	580·409	172292	O_{II}	B	2	939·22	106471	O_{I}	H
4	580·975	172124	O_{II}	B	4	948·73	105404	O_{I}	H
4	597·82	167274	O_{III}	B	4	950·17	105244	O_{I}	H
2	599·600	166777·9	O_{III}	B	4	952·36	105002	O_{I}	H
2	600·583	166505	O_{II}	B	2	952·96	104936	O_{I}	H
4	608·390	164368	O_{IV}	B	8	971·76	102906	O_{I}	H
4	609·828	163981	O_{IV}	B	5	973·26	102745	O_{I}	H
5	616·309	162256	O_{II}	B	5	973·92	102677	O_{I}	H
1	616·93	162093	O_{IV}	B	5	976·50	102406	O_{I}	H
5	617·064	162058	O_{II}	B	5	978·06	102249	O_{I}	H
3	624·609	160100	O_{IV}	B	4	978·62	102184	O_{I}	H
4	625·126	159968	O_{IV}	B	10	988·67	101146	O_{I} ?	H
4	625·848	159783	O_{IV}	B	10	990·13	100996	O_{I} ?	H
3	629·6	158823		M	10	990·73	100935	O_{I} ?	H
6	644·159	155241	O_{II}	B	7	999·47	100053	O_{I} ?	H
1	656·7	152276	O_{IV}	M-B	9	1025·84	97485	O_{I}	H
0	658·4	151883	O_{III}	F	8	1027·49	97324	O_{I}	H
5	672·913	148608	O_{II}	B	7	1028·21	97256	O_{I}	H
5	673·752	148423	O_{II}	B	1	1031·98	96901	O_{VI}	B-M
6	702·329	142383	O_{III}	B	0	1037·69	96367·8	O_{VI}	B-M
6	702·813	142285	O_{III}	B	8	1039·26	96222	O_{I}	H
6	702·905	142267	O_{III}	B	8	1041·00	96061	O_{I}	H
7	703·850	142076	O_{III}	B	7	1041·71	95996	O_{I}	H
7	718·495	139180	O_{II}	B	2	1134·6	88136		H
7	718·569	139165	O_{II}	B	10	1152·0	86805	O	H
4	758·685	131807	O_{V}	B-M	1	1199·8	83347		H
4	759·453	131674	O_{V}	B-M	10	1217·62	82128	O	H
3	760·232	131539	O_{V}	B-M	10	1302·27	76788	O_{I}	H
5	760·457	131500	O_{V}	B-M	10	1304·96	76630	O_{I}	H
4	761·131	131383	O_{V}	B-M	10	1306·12	76562	O_{I}	H
4	762·004	131233	O_{V}	B-M	0	1338·5	74711		M
0	774·3	129151		M	8	1355·73	73760	O_{I}	H
1	779·824	128234		B-I	5	1358·66	73601	O_{I}	H
6	787·716	126949	O_{IV}	B	1	1902·89	52552	O_{III}	F
6	790·205	126549	O_{IV}	B	1	1907·06	52437	O_{III}	F
6	796·665	125523	O_{II}	B	2	1916·48	52179	O_{III}	F

TABLE VI.—ALUMINIUM.

M = Millikan, " Phy. Rev.," 23, p. 1, 1924.
B-M = Bowen and Millikan, " Phy. Rev.," 27, p. 149, 1926.
B-I = Bowen and Ingram, " Phy. Rev.," 28, p. 444, 1926.
L = Lyman, 1st ed. of this work, and " Science," 60, p. 388, 1924.
P = Paschen and Sawyer, " Ann. d. Phy.," 84, p. 16, 1927.

I.	λ.	ν.			I.	λ.	ν.		
0	136·6	732332	O ?	M	4	1379·675	72481	Al_{III}	B-I
0	144·3	692809	O ?	M	4	1384·140	72247	Al_{III}	B-I
0	162·4	615839	O ?	M	10	1539·74	64946	Al_{II}	P
0	186·9	534988	O ?	M	1	1560·35	64088	Al_{II}	P
0	200·0	499950	?	M	1	1563·56	63957	Al_{II}	P
0	219·1	456413	O ?	M	1	1569·35	63721	Al_{II}	P
0	221·5	451508	O ?	M	1	1572·97	63574	Al_{II}	P
0	225·9	442693	O ?	M	2	1580·93	63254	Al_{II}	P
0	230·8	433332		M	2	1584·77	63102	Al_{II}	P
1	511·1	195656		L	3	1596·02	62656	Al_{II}	P
0	560·24	178495	Al_{III}	B-M	3	1599·44	62522	Al_{II}	P
0	656·7	152270	O_I ?	M	7	1605·764	62276	Al_{III}	B-I
0	658·4	151879	O_I ?	M	7	1611·858	62040	Al_{III}	B-I
3	695·82	143715	Al_{III}	B-M	4	1616·41	61866	Al_{II}	P
2	696·23	143631	Al_{III}	B-M	4	1618·38	61790	Al_{II}	P
0	725·74	137790	Al_{III}	B-M	3	1625·60	61516	Al_{II}	P
0	726·95	137561	Al_{III}	B-M	5	1644·15	60821	Al_{II}	P
0	802·0	124694		M	5	1644·78	60798	Al_{II}	P
3	854·98	116962	Al_{III}	B-M	6	1670·802	59852	Al_{II}	B-I
3	856·80	116713	Al_{III}	B-M	5	1681·78	59461	Al_{II}	P
1	892·00	112107	Al_{III}	B-M	5	1686·19	59305	Al_{II}	P
1	893·93	111865	Al_{III}	B-M	1	1718·3	58197	Al_{II}	L
1	935·20	106929	Al_{II}	P	4	1719·455	58158	Al_{II}	B-I
1	955·99	104613	Al_{II}	P	5	1721·273	58096	Al_{II}	B-I
1	990·88	100920	Al_{II}	P	5	1724·982	57971	Al_{II}	B-I
0	1048·83	95344·3	Al_{II}	B-M	5	1739·64	57483	Al_{II}	P
0	1050·01	95237·2	Al_{II}	B-M	2	1746	57273	?	
2	1142·97	87491	Al_{II}	P	1	1747·7	57218		L
4	1152·14	86798	Al_{II}	P	6	1750·56	57125	Al_{II}	P
3	1157·13	86421	Al_{II}	P	1	1751·7	57087		L
1	1158·14	86345	Al_{II}	P	4	1760·101	56815	Al_{II}	B-I
0	1162·59	86015	Al_{III}	B-M	4	1761·973	56755	Al_{II}	B-I
4	1177·48	84927	Al_{II}	P	5	1763·939	56691	Al_{II}	B-I
1	1179·38	84790	Al_{II}	P	4	1765·814	56631	Al_{II}	B-I
1	1189·07	84099	Al_{II}	B-M	4	1767·730	56570	Al_{II}	B-I
2	1190·07	84029	Al_{II}	B-M	2	1773·8	56376		L
2	1191·83	83904	Al_{II}	B-M	4	1776·9	56278		L
3	1208·35	82757	Al_{II}	P	4	1807·40	55328	Al_{II}	P
0	1209·25	82696	Al_{II}	B-M	3	1818·5	54990		L
1	1210·12	82636	Al_{II}	B-M	10	1828·61	54686	Al_{II}	P
1	1211·93	82513	Al_{II}	B-M	8	1832·87	54559	Al_{II}	P
4	1258·88	79436	Al_{II}	P	6	1834·82	54501	Al_{II}	P
6	1310·8	76330		L	1	1836·97	54437	Al_{II}	P
6	1319·4	75792	?	L	1	1838·27	54399	Al_{II}	P
6	1350·15	74066	Al_{II}	P	2	1839·64	54358	Al_{II}	P
2	1352·857	73917	Al_{III}	B-I	2	1848·90	54086	Al_{II}	P
2	1371·26	72925	Al_{II}	P	20	1854·715	53916	Al_{III}	B-I

TABLE VI.—ALUMINIUM (*continued*).

I.	λ.	ν.			I.	λ.	ν.		
8	1855·97	53880	Al_{II}	P	1	1926·99	51894	Al_{II}	P
5	1858·08	53819	Al_{II}	P	5	1930·03	51812	Al_{II}	P
3	1859·99	53764	Al_{II}	P	5	1932·43	51748	Al_{II}	P
20	1862·775	53683	Al_{II}	B-I	10	1934·54	51692	Al_{II}	P
1	1877·13	53273	Al_{II}	P	10	1934·75	51686	Al_{II}	P
3	1878·48	53234	Al_{II}	P	6	1935·881	51656	Al_{III}	B-I
2	1897·49	52701	Al_{II}	P	4	1936·96	51627	Al_{II}	P
4	1899·17	52655	Al_{II}	P	5	1939·30	51565	Al_{II}	P
2	1904·38	52510	Al_{II}	P	5	1945·35	51404	Al_{II}	P
4	1906·57	52450	Al_{II}	P	3	1960·70	51002	Al_{II}	P
5	1910·91	52331	Al_{II}	P	7	1962·67	50951	Al_{II}	P
4	1924·81	51953	Al_{II}	P	4	1965·23	50584	Al_{II}	P
2	1925·99	51921	Al_{II}	P	4	1990·534	50238	Al_{II}	B-I

TABLE VII.—CARBON MONOXIDE.

λ.	I.	N.	λ.	I.	N.
1335·0	1	74,906	1488·0	2	67,204
1339·0	1	74,683	1493·8	3	66,943
1343·0	1	74,460	1497·8	3	66,765
1353·6	1	73,877	1506·8	2	66,366
1356·1	2	73,741	1510·7	2	66,194
1361·3	2	73,459	1515·7	3	65,976
1368·0	1	73,099	1520·4	1	65,772
1371·8	2	72,897	1526·0	2	65,531
1374·1	2	72,775	1527·6	3	65,462
1378·1	2	72,564	1534·2	2	65,181
1384·4	1	72,233	1542·2	5	64,842
1386·4	1	72,129	1545·1	3	64,721
1392·2	1	71,829	1559·3	5	64,131
1395·7	2	71,649	1576·5	4	63,432
1401·1	2	71,372	1596·1	1	62,653
1404·0	1	71,225	1597·4	3	62,602
1405·5	1	71,149	1603·3	1	62,371
1409·0	2	70,972	1611·7	3	62,046
1411·4	1	70,852	1615·1	2	61,916
1414·0	1	70,721	1623·4	1	61,599
1419·0	2	70,472	1629·6	3	61,365
1426·1	3	70,121	1630·3	6	61,338
1435·6	2	69,657	1648·2	5	60,672
1438·7	1	69,507	1653·3	4	60,485
1443·7	1	69,266	1666·7	1	59,999
1447·0	1	69,109	1669·9	6	59,884
1452·4	3	68,852	1685·3	1	59,337
1463·7	3	68,320	1688·5	1	59,224
1473·0	1	67,889	1698·8	1	58,865
1475·4	1	67,778	1705·3	6	58,641
1478·0	2	67,659	1712·2	7	58,404
1480·9	2	67,527	1723·9	6	58,008

TABLE VII.—CARBON MONOXIDE (*continued*).

λ.	I.	N.	λ.	I.	N.
1729·5	8 *d*	57,820	1891·2	6	52,876
1743·5	3	57,356	1898·0	10	52,687
1747·3	7	57,231	1914·0	1	52,247
1774·9	8 *d*	56,341	1918·2	7	52,132
1785·1	6	56,019	1931·5	6	51,773
1792·6	10 *d*	55,785	1933·6	2	51,717
1801·9	2	55,497	1950·4	4	51,272
1804·9	8	55,405	1951·7	5	51,237
1811·0	10 *d*	55,218	1953·0	5	51,203
1825·7	7	54,774	1970·1	8	50,759
1830·1	9	54,642	1991·0	1	50,226
1837·2	1	54,431	2007·2	5	49,821
1841·3	8	54,309	2012·6	8	49,687
1846·7	2	54,151	2026·4	7	49,349
1849·4	4	54,072	2031·7	1	49,220
1859·6	10 *d*	53,775	2035·1	4	49,138
1870·3	3	53,467	2047·0	8	48,852
1878·5	10 *d*	53,234	2068·4	8	48,347

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APPENDIX I.

LIST OF PAPERS OF V. SCHUMANN.

Sensitization of photo-plates. Photo. Wochenblatt, p. 395, 1885; p. 49, 1886.

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APPENDIX II.

No better method for making the dry plates which must be used in the extreme ultra-violet has been discovered than that minutely described by Schumann in the "Annalen der Physik," Vol. V., p. 349, 1901. There is really nothing of importance which can be added to this description. There are some points, however, which it may be well to emphasize.

The three essential properties of a good plate are freedom from fog and streaks, high sensitiveness, and fine grain. Purity of material and extreme cleanliness are necessary to secure the first condition. The emulsion should be flowed upon fresh glass plates; old photographic plates, from which the emulsion has been removed, should not be employed. The gelatine itself (Nelson No. 1) should be fresh and free from dust.

The sensitiveness of the plates depends primarily on the length of time during which the emulsion is heated and the temperature at which it is maintained during this heating; a half-hour at 60° C. is recommended by Schumann. The temperature at which the plates are maintained during the time the emulsion is settling upon them also influences the sensitiveness to some degree. 18° C. is the correct temperature for this process. If the operation is carried on at 25° or 30°, the sensitiveness is somewhat increased, but the fatal fault of halation is introduced.

The three desired properties of a good negative depend greatly on the constitution of the developer, upon its temperature, and upon the time of development. I have tried the Pyrogallol-soda formula recommended by Schumann, Metol, Rodinol, and several other developers, but I prefer an

Ortol-potash developer made according to the formula of J. Hauff & Co., on account of its flexibility.

Solution A	Water	1000 parts.
	Metabisulphite of potash	$7\frac{1}{2}$ parts.
	Ortol	15 parts.
Solution B	Water	1000 parts.
	Carbonate of potash .	60 parts.
	Sulphite of soda (crystal)	180 parts.

I employ 15 parts A, 30 parts B, 20 parts water. The temperature is a most important factor. To secure uniform results, the developer is cooled to 3° or 4° and is kept on ice during development. For plates two or three months old, the time of developing is usually two to three minutes.

Strong developer at room temperature results in rapid development, which, in turn, produces negatives with a coarse grain and, ultimately, complete fog.

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